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A Dynamic Probabilistic Material Flow Modeling Method for Environmental Exposure Assessment

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Abstract

Simulation modelling is an important tool for assessing the environmental level of a pollutant. By modelling the flow of anthropogenic substances from the technosphere into the ecosphere and through several environmental compartments, the concentrations of these in air, water and soil can be estimated. These values are a fundamental requirement for any estimation of environmental hazard and risk posed by a chemical or substance.

In general, the input data needed for such models is uncertain and determining reliable values for environmental stocks and flows using a mass-flow model is a challenge. That is why Material flow Analysis (MFA) needs methods and tools to deal with this uncertainty. In static cases, this can be done via Probabilistic Material Flow Analysis (PMFA). But processes including time-dynamic behaviour cannot be handled with this. Therefore, the present thesis presents *Dynamic Probabilistic Material Flow Analysis (DPMFA)* as a new approach to close this gap. It includes:

- a mass balanced stock and flow representation,
- time-dynamic system behaviour and discrete period based time progress, and
- explicit uncertainty representation and propagation

In DPMFA, the existing Probabilistic Material Flow Analysis (PMFA) is linked to dynamic modelling means. In PMFA a system of dependent material flows is assumed to be in equilibrium for the investigated period (e.g. a year). Incomplete system knowledge is represented as Bayesian parameter distributions. On this basis, the dependent model variables (such as environmental stocks) are derived using Monte-Carlo simulation. To introduce dynamic behaviour of a system over a longer time span, in DPMFA, the flows of subsequent periods need to be calculated and the material accumulations in the sinks have to be added up. External inflows are considered for each period individually and intermediate delays are represented as stocks with specific release functions. As a result, environmental pollutant concentrations and exposures are determined based

on the absolute material amounts in stocks. In addition to the theoretical modelling approach, a respective modelling-package in Python was implemented and provided[1]. The tool enables application experts from different fields to develop models for their domain.

One important application field for this approach is the assessment of new substances such as engineered nano-materials (ENM), which are used in a growing number of products. At present, there are no analytic methods available to quantify environmental concentrations of ENM. Most of them are long-lasting, so they can accumulate in the ecosphere over a longer time period. This qualifies the modelling and simulation of ENM flows as suitable example of use to demonstrate the new approach.

We describe the development and application of DPMFA in the form of four scientific articles, which constitute the core of this thesis. Article I (Chapter 2) presents the specific requirements for the new modelling approach and implements a small example model using several existing modelling approaches to identify their possibilities and limitations. In article II (Chapter 3), the new approach is theoretically developed in detail and then exemplarily applied in a case-study to assess the environmental concentrations of Carbon Nanotubes (CNT) in Switzerland. The new approach is further specified in Article III (Chapter 4). In particular, the representation of incomplete knowledge from several data sources, model-robustness regarding design decisions, as well as sensitivity- and uncertainty analyses are discussed and resulting implications on the model and the investigated system are highlighted. A comprehensive application of the approach was performed in a modelling study in Article IV (Chapter 5). This way, the approach has been validated by applying it to realistic cases. These are modelling the concentrations of the materials nano-TiO_2, nano-ZnO, nano-Ag and CNT in the European Union. For each of the materials the concentrations in surface water, sediment, natural and urban soil, sludge treated soil and air have been estimated for the year 2014. Thereby, the appropriateness of the approach could be proved for the investigated class of exposure models.

[1] *https://pypi.python.org/pypi/dpmfa-simulator*

Zusammenfassung

Die Modellierung und Simulation von Flüssen anthropogener Substanzen aus der Technosphäre in die Ökosphäre und dort durch verschiedene Umweltmedien erlaubt es, die Konzentrationen dieser Substanzen in der Luft, im Wasser und in der Erde zu bestimmen. Die Kenntnis dieser Werte ist eine wichtige Voraussetzung für die Einschätzung von Umweltgefährdungen und Risiken, die durch diese Chemikalien oder Substanzen entstehen können. Eingangsgrößen für diese Materialflussanalyse sind die Flüsse zwischen den verschiedenen Bereichen. Jedoch liegen hierzu im Allgemeinen meist keine verlässlichen Werte vor. Daher werden zur so genannten Materialflussanalyse (MFA) Methoden und Werkzeuge benötigt, um diese Unsicherheiten entsprechend zu berücksichtigen. In statischen Fällen kann dazu die Probabilistische Materialflussanalyse (PMFA) herangezogen werden. Prozesse, die zeit-dynamisches Verhalten umfassen, können so jedoch nicht abgebildet werden. Daher wird in dieser Doktorarbeit die *Dynamic Probabilistic Material Flow Analysis (DPMFA)* als ein neuer Ansatz eingeführt, um diese Lücke zu schliessen. Er umfasst:

- eine massebilanzierte Repräsentation von Stocks (Lagern) und Flows (Flüssen),
- das zeit-dynamische Systemverhalten und den diskreten, periodischen Zeitfortschritt
- eine explizite Repräsentation und Propagation von Unsicherheit

In DPMFA wird die bereits existierende Probabilistic Material Flow Analysis (PMFA) mit der dynamischen Modellierung verknüpft. Dabei wird ein System abhängiger Materialflüsse innerhalb einer Periode (z.B. eines Jahres) als Gleichgewicht modelliert. Unvollständiges Systemwissen wird als Bayesche Parameterverteilungen abgebildet. Abhängige Modellvariablen (wie zum Beispiel Umwelt-Stocks) werden mit Monte-Carlo Simulation abgeleitet. Um auch das dynamische Systemverhalten über einen längeren Zeitraum abzubilden, werden in der DPMFA die Flüsse der aufeinander folgenden Perioden berechnet und die Material-Akkumulationen in den Modellsenken aufaddiert. Externe Zuflüsse

werden für jede Periode einzeln betrachtet und zeitliche Verzögerungen werden als Stock-spezifische Freisetzungsfunktionen abgebildet. Auf Basis der absoluten Materialmengen in einen Stock können nun Umwelt-Schadstoffkonzentrationen und Expositionen bestimmt werden. Zusätzlich zum theoretischen Modellierungsansatz, der im Rahmen dieser Arbeit erarbeitet wurde, wird ausserdem ein entsprechendes Modellierungs-Packages in Python zur Verfügung gestellt[2]. Dieses Werkzeug soll es Experten aus unterschiedlichen Bereichen ermöglichen Modelle für ihre jeweilige Anwendung zu erstellen.

Ein wichtiges Anwendungsfeld für DPMFA ist die Bewertung der Einflüsse neuer Substanzen wie zum Beispiel künstlich hergestellter Nanomaterialien (ENM), die in immer mehr Produkten Verwendung finden. Gegenwärtig gibt es kein analytisches Verfahren, um Umweltkonzentrationen von ENM zu bestimmen. Ausserdem sind viele ENM langlebig. Aus diesem Grund eigenen sie sich als Fallbeispiel, um den neuen Ansatz zu demonstrieren.

Wir beschreiben die Entwicklung und Anwendung von DPMFA in Form von vier Forschungsartikeln, die den Kern dieser Dissertation ausmachen. Artikel I (Kapitel 2) arbeitet die spezifischen Anforderungen, an den Modellierungsansatz heraus. Dazu wurde ein Beispielmodell mit unterschiedlichen bestehenden Ansätzen implementiert, um so deren Möglichkeiten und Limitierungen zu identifizieren. In Artikel II (Kapitel 3) wird der neue Ansatz zunächst theoretisch entwickelt und dann exemplarisch in einer Fallstudie zur Abschätzung der Umweltbelastung durch Kohlenstoff-Nanoröhrchen (Carbon Nanaotubes - CNT) in der Schweiz angewandt. Artikel III (Kapitel 4) behandelt weitere Aspekte des Ansatzes im Detail. Insbesondere werden die Abbildung unsicheren Wissens aus verschiedenen Datenquellen als Modellparameter, Untersuchungen der Modell-Robustheit gegenüber bestimmten Designentscheidungen sowie Sensitivitätsanalysen und Unsicherheitsanalysen diskutiert und sich daraus ergebende Implikationen für das Modell und das untersuchte System beleuchtet. Eine umfassende Anwendung der Methode findet in Artikel IV (Kapitel 5) statt. Auf diese Weise wird der Ansatz durch seine Anwendung in einem realistischen Szenario validiert, indem mithilfe von DPMFA Umweltkonzentrationen der Materialien nano-TiO_2, nano-ZnO, nano-Ag and CNT für die Europäische Union bestimmt werden. Für jede der Materialien werden die Konzentrationen in Oberflächenwasser, Sediment, natürlichen und urbanen Böden, Klärschlamm-behandelten Böden und in der Luft bestimmt und damit auch gezeigt, dass der Ansatz zur Expositions-Modellierung geeignet ist.

[2] *https://pypi.python.org/pypi/dpmfa-simulator*

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Contents

Part I.

Synopsis

1

Scientific framework of the thesis

The synopsis constitutes the frame of this thesis. It states the overall research problem and the scientific background, mentioning the some related word and identifying the gap the work intends to close. A set of solution objectives is defined to address the primary research problem. The scientific publications of this work fulfil one of the solution objectives each. The synopsis closes summarizing the achievements regarding the initial problem and the solution objectives, existing limitations, connecting points for future work and an overall conclusion.

1.1. Introduction

Mathematical models can help to investigate state variables that are hard to measure and are therefore an important tool in various disciplines. One example of use is simulation modelling of the flow processes of anthropogenic substances in the technosphere and the ecosphere. This allows the estimation of the levels of these substances in air, water and soil. However, to obtain reasonable values from these studies, appropriate modelling methods and tools are required.

The determination of these environmental flows and concentrations is a fundamental step in the assessment of risks and hazard posed by anthropogenic pollutants. While for many substances and environmental media, quantitative analytical measurements of the concentrations are not feasible, modelling and simulation methods can provide means for an alternative, indirect investigation. Therefore, the relevant processes of the system under study are represented in a model and the unknown variables can be estimated from this. With the help of simulation, the model enables conclusions about the original system, including the predictions about the past and the future and hypothetical scenarios (Figure 1.1).

In environmental exposure assessment, multimedia models are a well-established approach to pursue the environmental fate of a substance (MacLeod et al., 2010). The

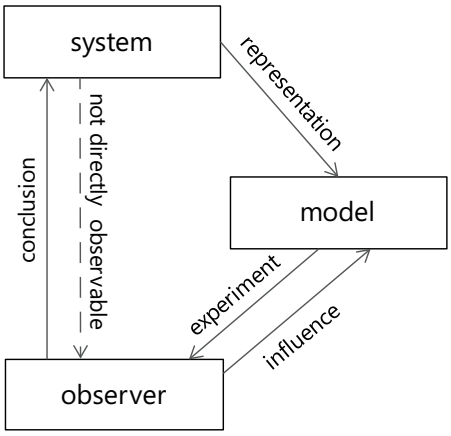

Figure 1.1: Schematic representation about the interaction between the original system, the model and the observer

term Multimedia in this context refers to environmental media (e.g. soil, air, surface water). Within the models, the different media of the system are represented as a set of separated model compartments, that allow the investigation on material transfers between them. Calculating the absolute mass flows, can now provide values for the model stocks (Baccini and Brunner, 1991). Furthermore depending on the investigated pollutant and the scope of the study, processes of the technosphere have to be taken into account. These could be material production, the application and use in different products, subsequent waste handling processes etc.

Once environmental stocks are estimated with the help of the model, this knowledge can be used for further risk analysis. The European Chemicals Agency provides a guideline on the calculation of the significant volume of an environmental media (ECHA, 2012) and based on this predicted environmental concentrations (PEC). The environmental risk assessment of the materials can then be performed by contrasting the PEC with the (eco)-toxicological properties of the material. This needs to be investigated for approval a new chemical for use in the European Union and is publicly available in the REACH-Database (Registration, Evaluation, Authorization and Restriction of Chemicals). Moreover, the basic mass flows can provide input parameters for environmental fate models, with a more detailed focus on mechanistic transformation processes. This has been done e.g. by Praetorius et al. (2012).

1.1.1. Engineered nano-materials as field of application

Engineered nanomaterials (ENM) constitute a well suited example domain for exposure assessment modelling. A particle is considered a nano-particle, if at least one of its dimensions has a size between 1 and 100 nm. In a nano-material at least 50 % of its particles have nano-particle dimensions and the term engineered refers to an intended production or design of this material (ECB, 2003). Over the last 1-2 decades their production volumes (Piccinno et al., 2012) and applications in products have massively grown (Future Markets, 2012) and as a consequence also the release of ENM to the environment.

Recently, some techniques to determine specific nano particles have been developed. These are for example Mitrano et al. (2012) using single-particle ICP-MS to detect silver and metal-oxide particles in waste water treatment plant effluent and Gondikas et al. (2014) identifying TiO_2 nano-particles from sunscreens in a bathing lake using electron microscopy and ICP-MS. Nevertheless, for most environmental media and nano-materials a direct measurement is not feasible Nowack et al. (2015). To enable an assessment, nonetheless, numerous material flow modelling studies were applied to determine the ENM flows to the environment, e.g. (Boxall et al., 2007; Mueller and Nowack, 2008; Gottschalk et al., 2009; Keller et al., 2013).

1.1.2. Probabilistic flow modelling

Most processes involved in the final material accumulation in an environmental stock are not precisely known. Using a single value for a model parameter from a diverse and conflicting set of assumptions means ignoring these uncertainties. This leads to simulation results whose actual value is indeterminable. To cope with the inherent data uncertainty about the model parameters, Gottschalk et al. (2010a,b) proposed Probabilistic Material Flow Analysis (PMFA). Therein, parameter uncertainty about an equilibrium flow model is represented as probability distribution and propagated through the model using Monte-Carlo simulation.

The PMFA approach has been applied to a wide range of materials and a rather large scope of investigated processes. The first study (Gottschalk et al., 2010a; Gottschalk and Nowack, 2011) just focused on nano-TiO_2, while later works expended the scope, covering nano-TiO_2, nano-ZnO, nano-Ag, Carbon Nanotubes (CNT) and fullerenes (Sun et al., 2014) and nano-TiO_2, nano-ZnO, nano-Ag, nano-$CuCO_3$, CNTs, nano-CeO_2, Quantum dots (QD), Carbon black (CB) (Gottschalk et al., 2015). Furthermore, it was applied in studies focusing on a rather narrow application like nano-Au from medical appliances

(Mahapatra et al., 2015). Other cases put the focus on particular technical processes like waste water treatment and subsequent sewage sludge applications (Sun et al., 2015) or the processes in a waste incineration plant (Walser and Gottschalk, 2014). Moreover, PMFA has been embedded in a risk assessment studies (Gottschalk et al., 2013a; Coll et al., 2016) taking the toxicity sensitivities of the affected species into account.

1.1.3. Dynamic flow modelling

For long-lasting pollutants time-dynamic processes come into play. These materials are not or only very slowly bio-degradable and accumulate in environmental media, such as soil or sediment. Also intermediate stocks, that re-release their materials with a considerable delay can have a significant impact on the emergence of the environmental concentrations. The in-use stock of substances in construction materials is a vivid example for the inherent delay over the life time of the building. They have an average time span of 80 years (ATD Home inspection, 2014).

PMFA includes an idealized flow model creating a stable state of simultaneous flows, that are assumed to be in equilibrium. Based on a large set of dependencies, a flow-matrix (Leontief, 1986) is calculated, distributing the model input to a set of sinks. Therefore, in the original formulation, no time dynamic behaviour is included. Sun et al. (2015) run their model for several subsequent periods and add up the model sinks for the total accumulated amounts. Walser and Gottschalk (2014) in addition used the output of one period's model inflow for a following one. Nonetheless, the approach is not suited to model realistic dynamic behaviour including the complex release behaviour from stocks over several periods.

1.1.4. Existing limitations and a new modelling approach

There exist other approaches and modelling tools that might cover the requirements to adequately reproduce and investigate the processes significant for the emerging environmental exposure. They base on dynamic system modelling (Forrester, 1961) and Bayesian modelling (Carlin and Louis, 2000). Müller et al. (2014) made a survey on a large range of existing dynamic modelling methods regarding their uncertainty handling. While more than 50 % do not consider uncertainty at all, only very few provided uncertainty handling using Gaussian error propagation (6 %) or using parameter ranges (5 %) but no full Bayesian uncertainty representation and propagation support was found. Bayesian networks and dynamic Bayesian networks (Daly et al., 2011) are most promi-

nent Bayesian models. Bayesian networks have already been applied to forecast environmental concentrations of engineered nanomaterials (ENM) (Money et al., 2012). Dynamic Bayesian networks, moreover, allow to model subsequent periods. However, these approaches do not provide a support for a mass-balanced flow modelling and the domain of the model variables and parameters is discrete and limited to a rather small number of states that all must be explicitly considered in the network transfer functions.

In the present work, we develop the so called Dynamic Probabilistic Material Flow Analysis (DPMFA). It is a key contribution to close this gap and provides a method to support prediction modelling for environmental concentrations of long-lasting anthropogenic pollutants. Therefore, in the following the requirements for the modelling approach are defined in detail and a survey on existing modelling approaches is given in Chapter 2. Having these methods and their functionalities and limitations in mind, we developed the new approach to assist application experts in the development of their exposure assessment models (Chapter 3). Besides, a modelling package developed in Python (Bornhöft, 2015) is provided to support the modelling work[1]. For the modelling package, also a tutorial is provided, explaining the model implementation (Appendix A). To facilitate the modelling and evaluation process, a rule-set is developed providing support on how to represent available data as model parameter. In addition, sensitivity and uncertainty analyses are discussed (Chapter 4). This dissertation finishes with a simulation study applying the DPMFA approach to determine environmental concentrations of several nano-materials for the European Union. This way the overall suitability of the modelling approach is validated on the example (Chapter 5).

1.2. Area of investigation & solution objectives

The overall investigation of this dissertation can be subsumed under the central research goal.

Research Question: How can we provide an approach for environmental exposure modelling that improves the prediction of stocks of anthropogenic pollutants in environmental media by including data uncertainty and time-dynamic processes?

[1] https://pypi.python.org/pypi/dpmfa-simulator

This main issue is addressed in the following solution objectives. In this dissertation each objective will be subject of one scientific publication.

1. **Review of existing modelling approaches.** The review of existing modelling approaches marks a preceding step to the development of the new one. It identifies their possibilities and limitations and sharpens the understanding of the actual methodological gap - revealing, what is missing in detail. Therefore, the review aims to cover the most promising existing modelling approaches as well as including a range of different features. This review should aim to provide an in-deep investigation about the existing approaches by implementing an example model using all of the methods to compare their specific characteristics.

2. **Development of the DPMFA modelling and simulation approach and a supporting software package.** The development of the DPMFA approach specifies, which system information are included in a modelling and simulation study and how they are represented. Based on this, the simulation mechanism has to be defined. The software package to support performing DPMFA studies has to implement the approach, providing a frame for the model development and components to execute and automate the simulation process. This includes addressing the targeted user group by choosing an programming language and architecture as well as planning the interaction between the users and the system. The aim of the implementation is to find a balance providing maximal flexibility, usability and software quality with a manageable implementation effort. Therefore, it is reasonable to apply well-established software development pattern like object orientation (Gamma et al., 1995) and simulation modelling pattern such as separation of model and experiment (Page and Kreutzer, 2005).

3. **Development of a guideline for modellers to represent uncertain data in the model and evaluate the simulation output.** The predictions made based on the model strongly depend on the interpretation of available uncertain data as model parameter. This data about a parameter value can stem from one or several sources, stating consistent or conflicting information and might be given in different form such as ranges, distributions or single values. Beside the predicted environmental stocks as main result of a simulation study, additional analyses can provide further insights. Sensitivity and uncertainty analyses help identifying the most influential factors for the emergence of a stock and the main sources of

uncertainty. Including these steps into the modelling and evaluation process can improve the quality and the expressiveness of the findings obtained in a simulation study. This objective aims to provide a rule-set on how to prepare the available data in a formalized way in the model creation, on how to prepare and perform the simulation studies, and on how to interpret simulation results and perform sensitivity and uncertainty analyses.

4. **Validation of the suitability of the approach by applying it to real-world examples.** The validation of the appropriateness of the approach and the supporting software package will be performed by applying them in exposure modelling case-studies. To demonstrate the suitability of the new modelling approach, the respective studies need to encompass both data uncertainty and time-dynamic system behaviour. Moreover, the case-study should estimate environmental concentrations of pollutants, which are relevant for risk assessment due to their abundant use and a potential hazard.

1.3. Overview of the investigation

Main contributions presented in this cumulative PhD-thesis are compiled from four peer reviewed research papers. Three of the papers were published (II & IV) or submitted (III) to international peer-reviewed journals. Paper I has been published as peer-reviewed conference contribution in the proceedings of an international conference. In paper IV, which contains the application of the modelling approach on a study of different ENMs in the EU, I am co-author of my colleague Tianyin Sun, an environmental scientist, who is an expert for the investigated processes.

Each articles marks a step in the development of the new method and addresses one of the solution objectives. In the following, I sketch the focus of each of them, describe their function as part of the overall research question and summarize the performed work and the main findings.

1.3.1. Review of existing modelling approaches.

The solution objective to perform a review of existing modelling approaches for exposure assessment is addressed by the first publication of this work:

Article 1: Material Flow Modelling for Environmental Exposure Assessment - A Critical Review of Four Approaches Using the Comparative Implementation of an Idealized Example

The article (Chapter 2) presents the technical requirements for a material flow modelling to assess environmental pollutant concentrations, including time-dynamic behaviour and explicit uncertainty representation. A simple example case has been implemented using several modelling approaches. It includes uncertainty and time dynamic behaviour and with the help of this comparison, the individual strength and limitations of the different methods have been identified and the methodological gap has been revealed.

We introduce the area of mass-flow modelling and its application in environmental risk assessment (MacLeod et al., 2010; Klaine et al., 2012; Mueller and Nowack, 2008) and discuss uncertainty representation in the model Pate-Cornell (1996); Refsgaard et al. (2007) and its propagation to dependent variables. Then, in a pre-selection four modelling approaches and tools that appeared particularly promising for the modelling work have been identified: Probabilistic Material Flow Analysis (Gottschalk et al., 2010a) already proofed its suitability in a series of non-dynamic studies. Vensim for System Dynamics modelling (Forrester, 1961) has been widely used to simulate continuous systems. Umberto (ifu Hamburg GmbH, 2014) and STAN (TU Vienna, Institute for Water Quality, Resource and Waste Management, 2012) support graphical flow modelling, Umberto originating from Material Flow Networks (Möller, 2000) and STAN from Material Flow Analysis.

The example system was designed to include a static structure of one external source to the model, a flow compartment splitting the incoming flow to a model sink, and a stock, that is connected to a second model sink (Figure 2.1). The model is simulated over a time period of 5 years. The external inflow to the model as well as the split of the stream to the subsequent compartments are modelled as probability distribution functions to represent incomplete system knowledge. For the inflow, an empirical distribution is assumed and for the rate of the splitting of the incoming flow a normal distribution function. For the delay function of the stock also an empirical distribution is used to distribute the material release of the future for the incoming material over the next periods.

The modelling approaches are evaluated with respect to what extend they are able represent the normal as well as the empirical distribution for the parameters under uncertainty and for the empirical distribution defining the delay. The results of the

comparative analysis (Table 2.1) indicate that PMFA and Vensim are most suitable to represent the given example, but have some deficits as well.

1.3.2. Development of the DPMFA modelling and simulation approach and a supporting software package

The development of the DPMFA as a new modelling approach and its implementation as a software package are subject of the second contribution (Chapter 3).

Article 2: A Dynamic Probabilistic Material Flow Modelling Method

First, the theoretical modelling approach is introduced as a mathematical model. Based on that, the modelling software package is implemented in Python. Finally, an existing steady-state exposure model is re-implemented with the presented approach and later extended for a dynamic case as a proof of concept. This paper provides foundation for the model development, technical implementation and evaluation.

The elements of the static model structure (Section 3.2.1) are presented as model compartments. They include **external inflows** to the system, **flow compartments** that split an incoming flow to several outgoing ones, **stocks** that store incoming materials and re-release them later and **sinks** as final accumulation points.

The parametrisation of the model inflows defines absolute values for every period individually. Stocks include a delay function that schedules shares of the incoming material for re-release in future periods. Transfer Coefficients (TC) define the relative share of the total outflow from a flow compartment or a stock (Eq. 3.1). System uncertainties are represented as probability distributions in the respective model parameters. Both distribution functions and empirical distributions are possible. We consider system uncertainties for the transfer coefficients and the absolute model inflow values.

The general DPMFA simulation mechanism is structured as a 3-layered process (Figure 3.2).

- The **"immediation flow layer"** calculates the absolute flows of one period. Therefore, a flow matrix A is assembled from all TCs of the model (Eq. 3.2). The material inflows to the flow matrix for the period are defined as inflow vector I (Eq. 3.3). The accumulation for all compartments X is determined by the flow matrix for the inflow (Eq. 3.4)
- The **"dynamic flow layer"** accounts the stocks over the simulated time. At the

beginning of every period, the inflow vector of the period I is determined from the external input of the system and the releases from the stocks. Then, the global flow calculation on the immediate flow layer is performed. Subsequently, the material accumulations determined in the flow calculation are stored to the stocks and sinks. Future material releases from the stocks are calculated based on the current accumulation and their delay functions and scheduled for the later periods (Eq. 3.5 - 3.10).

- On the **"Bayesian layer"** the Monte-Carlo simulation is performed. For the given sample size of the simulation study, random values are drawn from the parameter distributions. For each parameter set, the dynamic flow system is simulated once. The simulation results over the whole sample size have to be statistically evaluated afterwards.

We implemented the approach as software package in Python. The package consists of two main parts:

- A `Simulator` to perform experiments and statistically evaluate a `Model` using the previously described simulation mechanism. The `Simulator` is a black box component that is used "as it is" and just needs to be parametrized with the number of investigated periods and the sample size.

- The `Model` has to be specified by the modeller performing the study. Therefore, a set of white-box components needs to be specified and assembled to represent the intended system behaviour. These components are abstract classes, which the user implements to reproduce a specific system.

The new package was used to first re-implement the steady-state exposure model by Sun et al. (2014) to validate it for the static case. It was shown that the exposure model for CNTs in Switzerland could be reproduced (Table 3.1). In a second step, the model was extended including information about the production volumes over the years and projected the production growth of the past years to predict the future development. Some applications of CNTs cause considerable residence times in the technosphere. This was modelled by in-use stocks. With this model, we calculated the CNT stock in soil for Switzerland for the years 2014 and 2025 (Figure 3.9) and determined Predicted Environmental Concentrations (PEC) of 74 ng/kg for 2014 and 486 ng/kg for 2025.

In an alternative scenario, we simulated, the hypothetical case of an immediate ban on CNTs (Figure 3.11). Here we could track the slow decrease of the in-use stocks and

a stabilisation of the model sinks. For this case a PEC of 192 ng/kg for soil in CH for 2015 was determined.

1.3.3. Development of a guideline for modellers to represent uncertain data in the model and evaluate the simulation output

The third paper (Chapter 4) focuses on specific aspects of the modelling and the evaluation process of the new method.

Article 3: Representation, propagation and interpretation of uncertain knowledge in dynamic probabilistic material flow models,

It highlights the representation of incomplete knowledge from different sources as parameter distribution. Furthermore, sensitivity analyses to assess the impact of particular parameters on the model output are discussed and uncertainty analysis to determine the contribution of the individual uncertainty the parameters on the model output are investigated. As the main contribution a guideline is developed that summarises key modelling and evaluation steps. Compared to the investigations in Chapter 3, here we consider DPMFA modelling studies with a broader scope and discuss the steps before and after the pure technical simulation of the model.

The modelling and evaluation processes are explained on the example of an adapted version of the CNT exposure model from Article II (Chapter 3).

At first, we suggest set of rules related to data fusion on how to represent data from a single source as a probability distribution. Data provided as ranges are represented as uniform distribution over the given range. For data from sources giving only single values, an implicit range is added as support. These values are modelled as triangular distributions. Afterwards, random samples from all distributions are created and added up to a combined one. The sample size of each single distribution is defined based on the distribution's degree of belief (DoB). This DoB determines the relative credibility of the underlying data source compared to the other data sourced include in the combined sample (Smets, 2007; Destercke et al., 2009). Criteria for the credibility could be for instance the validity or acceptance of the applied methods or a peer-review process. For the given example, we discuss the production volumes as well as the relative transfer coefficients as uncertain parameters.

Next, the model output is calculated with the determined parameter distributions. These are for the given example the material stored in in-use stocks, environmental

stocks, and technical compartments for the years 2012 and 2020 (Table 4.1). For the outputs of interest, we recommend to perform a sensitivity and uncertainty analysis. In the example, they have been executed for the sediment stock.

Sensitivity analysis are a proven way to identify the impact of specific parameters on a model output variable. Sensitivity coefficients (Eq. 4.1) calculate the correlation of the change of a model parameter and the investigated output variable. In this way, the impact of the parameter can be determined. We discussed the specific characteristics of the sensitivity analysis for DPMFA models. Thereby, different domains of the output variable, the parameter values as well as their comparabilities and the stochastic nature of the model were taking into account. Afterwards, it is possible to identify the parameters with the highest impact on the output of interest.

The model uncertainty was assessed the evaluation of uncertainty ranges (Eq. 4.2). This way, the impact of the parameter uncertainty of the individual model parameters on the uncertainty range of the sediment as output variable is determined (Figure 4.5). In the example, the production volume and the Sewage Treatment Plant (STP) efficiency were identified as the largest uncertainty sources for the model output variable and further investigated in scenarios based on the respective .05 and .95 quantiles from the parameter distributions.

Finally, the performed and explained modelling and evaluation steps are summarized in the form of a guideline that states the aim for each step in the global context of the study and the specific features of performing them in DPMFA (Table 4.5).

1.3.4. Validation of the suitability of the approach by applying it to real-world examples

In the fourth paper (Chapter 5) the DPMFA method is applied to predict current and future concentrations of several ENMs for the European Union.

Article 4: Dynamic Probabilistic Modelling of Environmental Emissions of Engineered Nanomaterials

It serves as the validation for DPMFA and aims to prove that the approach is well suited for the prediction modelling of environmental pollutant concentrations. The subject of the work is the prediction of past, current and future flows of the ENMs nano-TiO_2, nano-ZnO, nano-Ag, and CNT for the European Union and the material accumulations in the individual environmental compartments and the in-use stocks. The

investigation of nano-Ag takes into account that the application of "silver colloids" has a long history as biocide (Nowack et al., 2011) and can be seen as nano-Ag as well. Therefore, two scenarios have been modelled for nano-Ag, one that includes the historical use and the other one without.

The applied DPMFA model reproduces the pathways of the ENMs from their production over the distribution in different products, release from the products and subsequent flows towards a final accumulation in an environmental media. One particular focus of the model is the release dynamics of the ENMs from the in-use stocks. Here, we make a distinction between the material release during the products in-use phase and at the time after the end of the product life. These two different release types from the same product category do not only differ in the release times, but also in their pathways. For instance, the release of nano-Ag from textiles during their use-phase is heading partly to waste water and partly direct to the environment. In contrast, at the end of life, there are land-filling, waste incineration, recycling and further export processes (Table 5.1). For each relevant product category the ENM is applied in, we model the ENM releases for the use-phase of the products and for its end-of life (Figure 5.2).

The distribution model specifying the material transportation after the release from the product was adapted from Sun et al. (2014). Annual production volumes were estimated based on a literature surveys on the production volumes of the different ENMs (Table C.1) and the technological development of ENMs (Table C.2). The study was able to reproduce the ENM stocks and flows, trace the accumulated materials over time (Figure 5.3) and provide PECs for the EU in 2014 for the environmental media "surface water", "sediment", "natural and urban soil", "sludge-treated soil" and "air".

Finally, we discuss the comparability of these values with findings from studies using PMFA such as Mueller and Nowack (2008); Gottschalk et al. (2009, 2013b); Sun et al. (2014), their value as input for environmental fate models Praetorius et al. (2012), and their use in the context of environmental risk models that contrast them with ecotoxicological effect concentrations (Gottschalk et al., 2013a; Holden et al., 2014).

1.4. Achievements & contributions

This work contributes a new modelling method, and therefore a suitable tool to improve environmental exposure assessment. With the new "dynamic probabilistic material flow analysis" (DPMFA) method environmental concentrations of long-lasting anthropogenic pollutants can be estimated, where direct analytical methods for a quantitative measure-

ment are not feasible. Compared to modelling methods used so far, the one proposed in this work allows more precise and reliable predictions, because it

1. comprises the reproduction of mass-balanced material transfers in a model,

2. regards the time-dynamic behaviour of these flows over time to calculate the accumulation of absolute material stocks and

3. explicitly includes and propagates incomplete system knowledge.

Therefore, in a first step the the requirements for the indirect assessment of anthropogenic pollutants in the environments have been identified. Taking these requirements into account, the capabilities and limitations of existing methods were evaluated and the methodological gap determined. The DPMFA method was developed to close this gap. It was formalized and described in a general way and implemented as a simulation framework in the programming language Python. The package provides support for domain experts from different fields in creating simulation models to investigate their specific systems. In addition, the guideline was developed to represent, propagate, and interpret uncertain knowledge in DPMFA models. It provides a larger frame around the technical core modelling approach and gives more detailed advice, how parameter distributions can be generated out of a diverse set of data sources. Furthermore, it provides a stepwise strategy to interpret simulation results and perform sensitivity and uncertainty analyses. Finally, the method was applied to assess the environmental concentrations of several engineered nanomaterials. This way, the suitability of the approach was proved on a set of real-world examples.

1.5. Validation

The validation of new methods, and models is a crucial step in scientific work. Demonstrating their correctness and the appropriateness of the underlying assumptions determines the legitimacy of all obtained results and findings.

In this thesis we applied validation steps on different levels and with different scopes:

- **Appropriateness of the new approach.** The central aim of this work is to provide an appropriate solution for the identified gap in the modelling methodology for exposure assessment. In Article IV (Chapter 5), we showed that appropriateness of the new approach by applying it to to a real life example. Furthermore,

my Phd-work was settled as an interdisciplinary cooperation between the Environmental Risk Assessment and Management (ERAM) group at Empa, where I worked as a PhD-researcher and the Informatics and Sustainability group at the University of Zurich. In the ERAM group, I was part of the EU-Project "Marina - MAnaging the RIsks of NAnomaterials"[2] with the aim to develop methods for exposure assessment. This way, the modelling approach has been developed in close coordination between the modelling and the application experts. Therefore, the requirements taken into account for the new approach directly refer to the needs from applied exposure modelling.

- **Correctness of the software package.** The DPMFA approach and the supporting software package are based on techniques that all are well-established such as mass-balanced models, Bayesian modelling, Monte-Carlo simulation, dynamic modelling and Probabilistic Material Flow Analysis. The mathematical foundation of the developed approach has been detailed documented (Section 3.2) in publication and is therefore comprehensible. The programming package was implemented using well-established packages for the actual statistical computation; in particular numpy (NUmerical PYthon) was used for the matrix calculation (van der Walt et al., 2011). Furthermore, we validated the package for a static case against the steady-state model of Sun et al. (2014) that was implemented in the language "R" (R Development Core Team, 2012), and had already been published previously.

- **Validity of the application models.** It is a key characteristic of Bayesian models that they cannot be validated in terms of checking the model output against a measured value. The parameter distributions of Bayesian models accept to contain false values, to ensure that the true value is covered. As soon as some of the underlying assumptions of the model can be proved or rejected, the respective parameter distribution becomes narrower and as a consequence the simulation results more certain. Nevertheless, in cases that do not allow a direct validation these models are our best instrument.

  Therefore, the data collection and evaluation process has to be comprehensive and reliable. Due to that issue, a major share the time and effort spend on the modelling works of the application paper (Chapter 5) was on data survey and assessment to provide a comprehensive investigation.

[2]MARINA project - Grant Agreement n° 263215, *http://www.marina-fp7.eu/*

1.6. Limitations

This section lists a set of limitations of the DPMFA approach. They include limitations by design that are the result of the abstractions and limitations defined for the model. Other limitations cover aspects that have not been in the focus of this thesis and could be subject to future work.

1.6.1. Intended abstractions from the real system

The abstractions made from the system under study aim to represent only the major aspects of the system to reduce the model complexity and enable the computation of relatively large models. This limits the applicability for analyses with a different focus:

- **Deterministic, period-based time progress.** One of the design decisions, we have made while shaping the modelling approach, is its time representation. Time progress is represented as deterministic equidistant steps (years in the application models) and in each step all flows are calculated for that period. For the investigated cases, this is a useful assumption, because data usually is available on an annual basis (e.g. production volumes or product use phases). Therefore, continuous processes can only be represented with a granularity of the period length.
- **Deterministic delay functions.** Delay functions define how long a particular share of material is stored after entering a stock before it is re-released. In the approach, they are deterministically modelled. This reflects the fact that the uncertainty about accumulated material is mainly caused by the uncertainties of the absolute system inflows and the way a material takes. The uncertainty about the residence times has less impact.
- **Constant transfer coefficients.** TCs determine the material share that is heading towards a particular target compartment as part of the total outflow of the compartment. They are defined as probability distributions representing inherent system uncertainties. At present, they are kept unchanged over the whole simulation period.
- **Well-mixed compartments.** In the chosen modelling approach, all material in a stock or a sink is indistinguishable, regarding its age or the pathways taken through the system. In cases, where material needs to be differentiated by certain criteria, respective stocks have to be introduced to the model.

1.6.2. Increased requirements for model development and simulation

In comparison with other less complex modelling approaches, the DPMFA approach poses higher requirements on the model development, calculation, and evaluation. This limits its use in cases where the obtained benefits are not supposed to prevail the additional effort.

- **Required abilities.** Performing a simulation study with DPMFA, the modeller needs special abilities. In the first place, an understanding of the modelling approach and in particular a basic understanding of the underlying Bayesian statistics is required. Furthermore, basic programming skills in the language Python are necessary for the model implementation.
- **Modelling effort.** The modelling effort to create a DPMFA model is higher, compared to deterministic and non-dynamic approaches. As inputs for a DPMFA model, annual information about the system inflows and delay-functions for all model stocks are needed. Furthermore, model parameters under uncertainty require a more extensive data collection process to include all relevant informations. Also, the sources the data originates from need to be assessed about their credibility and the relevant information has to be combined to one parameter distribution.
- **Computational effort.** Due to the Monte-Carlo simulation process for calculating the model, the computational effort can become a limiting factor. With a rising degree of freedom (i.e. the number of independent probability distributions of the model parameters), also the required sample size increases.

1.7. Future work

Future work on the DPMFA modelling approach could address its application for further exposure assessment modelling, an improvement of the user interface, the development of more application specific model components and the improvement of the used sampling method. Furthermore, time dependent transfer coefficients could be introduced.

Application in further exposure assessment studies: At present, the approach developed herein has been applied in two studies to model engineered nano-materials (Sun et al., 2017, 2016). Future work could continue gathering data to improve the predictions made by these models, once new information is available. Also, the model could be revisited, if the investigated processes change fundamentally e.g. regarding production volumes or waste and sewage treatment processes. Furthermore, the approach

can be used for its intended purpose – performing further modelling and simulation studies for a wide range of anthropogenic pollutants. There, also fate modelling, including degradation and mechanistic transformation processes, a more detailed look on regionalization could be taken into account.

Appending of a more convenient user front-end: A potential evolution of the modelling package could introduce a better user interface. This could significantly lower the barriers to entry for users without programming skills. In general, two variants are conceivable, either using a spreadsheet program (e.g. Microsoft Excel) or the development of a graphical front-end to compose models as a set of boxes and connectors, which can be subsequently parametrized. However, while these extensions of the existing package are suitable to significantly simplify the modelling process and open it for use on a larger scale, it also introduces limitations to the large flexibility provided by the implementation as python package.

Development of application-specific components: Future work could also extend the modelling package with application specific components. The model components (`Stock`, `FlowCompartment` etc.) inherit the simulation specific functionalities from abstract super classes. This allows to extend them just for the application specific behaviour and keep the interactions unchanged. Instead of modelling a compartment "Waste Incineration Plant" (WIP) by instantiating a `FlowCompartment` (or a `Stock`) and setting `Transfer`s to connected compartments and parameters, the modeller could directly create a respective WIP object and also get default parameter values. A set of specific components could further be provided as package to increase their re-usability and the comparability of the simulation results.

Application of a different sampling technique: Finally, the applied sampling method could be reconsidered. Instead of Monte-Carlo Simulation more complex approaches, such as Latin hypercube sampling (LHS) (McKay et al., 1979) could reduce the required sample sizes significantly, in particular for models with a large number of degrees of freedom. In Monte-Carlo sampling a random sample of size n is drawn from a distribution by creating n *independent* random values from the *domain* of the distribution and mapping them with the probability *density* function.

LHS performs a "stratification" of the probability distribution. To draw a sample of size n, the *range* of the cumulative probability distribution is subdivided into n equal intervals. For each interval exactly one random value from the respective range of the *domain* is taken and mapped on the probability *density* function. This way the sample much faster converges against the underlying distribution. However LHS needs more computational time and memory to sample a value, due to first calculating all intervals

on the cumulative density function. Therefore the real computational improvement would require further investigation.

Introduction of time dynamic TCs: At present, time dependent changes of TCs are not represented in the DPMFA. This is a suitable simplification for most processes investigated in exposure models where it represents inherent process characteristics that do not change over time such as the water-solubility of a material. Therein, changes primarily result from external model inflows for instance due to production volumes. However, systems and scenarios exist, where changing TCs could be desirable. Examples are improved removal processes in Waste Water Treatment Plants (WWTP) over the years or altered fields of application for an existing substance. Future work could adjust the modelling process to revoke this limitation.

1.8. Conclusion

Incomplete knowledge and complex long-time material release and accumulation processes have often hindered reliable predictions about the level of anthropogenic pollutants in environmental media using a mass-flow modelling methodology.

This work has presented Dynamic Probabilistic Material Flow Analysis as an approach to determine environmental concentrations of pollutants in cases where previously modelling approaches could not provide a clear estimation. Since these values are fundamental for the assessment of environmental risks and hazards posed by the substances, the new DPMFA approach constitutes a valuable supplement for the environmental modeller's tool-kit.

The implementation of the software package supporting the modelling and simulation approach and making it available as python package creates the basis for serving other scientists in their modelling work. Moreover, thanks to the close cooperation in my group, including environmental scientists, the approach could be tailored considering their requirements. This way, the case-study investigating different nano-materials for the European Union (Chapter 5) marks both a validation for the appropriateness of the DPMFA approach for environmental modelling and an important step in the environmental exposure assessment of nano-TiO_2, nano-ZnO, nano-Ag and CNTs.

The increased modelling effort as well as long calculation times for large models and the required Python skills of the model developers can limit the application of the modelling package in some cases. However, future work could address these issues introducing new sampling methods and a user front-end to reduce this limitation. Nonetheless, in

cases of long-lasting substances and considerable data uncertainties DPMFA provides an alternative to previous methods. This alternative should be taken into account for exposure modelling.

Part II.

The Contributions

2

Critical Review of Existing Flow Modelling Methods for Exposure Assessment (Paper 1)

Original publication:

Material Flow Modelling for Environmental Exposure Assessment - A Critical Review of Four Approaches Using the Comparative Implementation of an Idealized Example

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Abstract

Newly developed materials such as engineered nanomaterials are produced in increasing amounts and applied in a growing number of products. Once released to the environment, they can pose a hazard to ecosystems and human health. To assess potential risks, the exposure of the material to humans and the environment has to be determined. For many materials such as engineered nanomaterials, a quantitative measurement of environmental concentrations is not feasible. Material flow models can be used to determine these concentrations indirectly by predicting material flows in the environment. Several modelling approaches can be applied to represent existing knowledge about the flows of materials into and between environmental media or compartments and to consider the uncertainty and variability of the input parameters. In this study we evaluate four existing approaches with regard to their capabilities for indirect exposure assessment, focusing on their ability to treat uncertainty. We first explain how we preselected the

four most promising modelling approaches: material flow analysis, system dynamics, material flow networks, and probabilistic material flow analysis. We then define a set of evaluation criteria based on the requirements of environmental exposure assessment and develop a simplified example system that is designed to test these criteria. Based on the comparative modelling and implementation of the example system, we discuss the capabilities and limitations of the approaches and indicate what is missing for a reliable environmental exposure prediction using material flow modelling.

2.1. Introduction

A main issue in the risk assessment of new substances such as engineered nanomaterials (ENM) is to determine the exposure of humans and ecosystems to the substances. An understanding of the environmental fate of a chemical product leads to knowledge about actual environmental concentrations, exposures and potential risks (MacLeod et al., 2010). For many pollutants, a direct measurement of environmental concentrations is not feasible and so the environmental fate cannot be determined directly. Material flow modeling holds the opportunity for an indirect assessment (Klaine et al., 2012). Instead of a direct assessment of environmental concentrations, material transfers between environmental compartments are regarded. This enables an estimation of material accumulations in the respective compartment and so the prediction of environmental concentrations based on standard sizes for environmental compartments (ECHA, 2012).

Even though material flow modeling provides means for environmental exposure assessments, the informative value is usually limited by incomplete knowledge about some system parameters. This uncertainty results from variances of the actual flows and the partial or total lack of knowledge about their true behavior. (Pate-Cornell, 1996; Refsgaard et al., 2007) To obtain reliable results, it is essential to consider these uncertainties, represent them explicitly in the flow model and process them through the model, using an adequate simulation method.

Another important issue is that temporal delays should be adequately represented in the model. The transfer of a pollutant from the point where it is released to the environment to the area where it finally accumulates is usually not immediate. Often, a material is bound for a long time in a compartment before it is further transferred through the system and finally accumulates. To investigate such system behavior appropriately, a modeling approach must be able to represent a time dynamic behavior and delayed material release from local stocks.

A good example for the use of material flow modeling for an environmental exposure assessment is found at Mueller/Nowack 2008. These authors used a methodology related to material flow analysis (MFA) to assess environmental concentrations of several ENM. Gottschalk et al. (2010a) extended the classical MFA approach to probabilistic material flow analysis (PFMA) by the introduction of Bayesian statistics to represent and process uncertain knowledge about system parameters. Besides MFA and PMFA, System Dynamics (SD) and Material Flow Networks (MFN) appear to be suitable for a comprehensive exposure assessment using material flow modeling.

In this study we provide a detailed look on several most promising material flow modeling approaches. In particular, we will highlight the capabilities and limitations of each modeling approach to represent uncertain knowledge about system parameters and time dependent release behavior from local stocks.

For our investigation we first preselected the most promising modeling approaches. Then, we developed an idealized example system that comprises the most crucial aspects of exposure assessment modeling. Finally, we implemented the example system using each of the modeling approaches and based on that evaluated the specific capabilities and limitations of the approaches.

2.1.1. Selection of material flow modeling approaches

The selection of the approaches to study was based on two principles: The expected capability of an approach to represent a system of material flows to predict environmental concentrations and second, the coverage of a large variety underlying modeling and simulation mechanisms. That way, four approaches were chosen for further examination. System Dynamics was developed to represent dynamic systems as sets of material stocks and flows, interconnected by information flows. The approach allows a quasi-continuous simulation by numerical integration with Euler- or Runge-Kutta-methods (Morrison, 1991). The original approach was developed by Forrester (1961). There are several software tools available to support System Dynamics modeling and simulation such as DYNAMO compilers and graphical modeling tools such as Stella. We used Vensim for the exemplary model. Material Flow Networks are based on Petri Nets. They are mainly used to account material flows in operational processes, in particular Life Cycle Assessment. Based on the production of goods the dependent substance and energy flows are determined. The approach was developed by Möller (2000) and extended by Wohlgemuth (2005) and is supported by the graphical modeling tool Umberto. It was used for the implementation of the example. Material Flow Analysis (MFA) is

an approach to model material flows as period-oriented transfer of a material between system entities (Brunner and Rechberger, 2004). The main aspects of MFA are included in the software tool STAN , with which we performed the exemplary implementation. The approach was developed by Baccini and Brunner (1991). Probabilistic Material Flow Analysis (PMFA) is a modeling approach that was specifically designed for environmental exposure modeling (Gottschalk et al., 2010a). It extends the classical MFA approach by Bayesian statistics. It describes a stable state in a system of dependent material flows under substantial uncertainties. There is no software program directly implementing the approach. Instead the language R for statistical computing and graphics and some packages that extend it provide the modeling methods.

2.1.2. Developing evaluation criteria

The criteria to evaluate the different modelling approaches are chosen to reflect crucial requirements of material flow modelling to predict environmental concentrations. Of particular interest are the way how uncertain knowledge is represented and processed and how complex and time dependent release from stock is modelled. The first evaluation criterion regards the capability to represent and process incomplete knowledge. Usually, the existing knowledge about the actual behavior of a specific pollutant released to the environment is not complete. There is uncertainty about its release, about the flow rates between the compartments of the system, and about the accumulation and degradation rates of the material. The Bayesian concept of probability enables the full representation of uncertain knowledge as different assumptions with different degrees of credibility. (Cullen and Frey, 1999) Thus, an adequate system representation in the model and meaningful simulation results should display uncertain information as Bayesian probability distribution. Depending on the knowledge about the process that needs to be examined and the way the information was gathered, usually they are available as theoretical or empirical distribution functions. We evaluated the modeling approaches including both variants. The second evaluation criterion regards stocks and their ability to represent a dynamic system behavior over time. Usually, the emergence of environmental contamination from a released pollutant is not an immediate process. For instance, a pollutant can be bound in a landfill for several years before it actually reaches ground water. The approach should be able to deal with such a delayed release. The modeler should be able to consider a rate of the total amount stored, a time delay, or external triggers as conceivable factors for a release from a local stock. Additional attention is paid on the modeling and simulation process, in particular how they are

performed with each approach and what support and guidance the respective software tools provide.

2.2. Definition of the example system

The aim of this study is to evaluate the modelling approaches with regard to the previously defined criteria. Therefore, an idealized example system was developed for comparative implementation. The properties of the system to be modelled are derived from the evaluation criteria. Thus, the fulfilment of a criterion can be assessed by the adequacy with which the corresponding aspect of the system could be implemented. Beside the requirement to comprise the characteristic aspects of flows of pollutants in the environment, the system should be kept simple in size to avoid unnecessary modelling effort and a concealing of the actual modelling and simulation principles of the approach. The basic system consists of several compartments, a source releasing material, relative flows between the compartments, material accumulation, and a stock with a time delayed release of material (Figure 2.1).

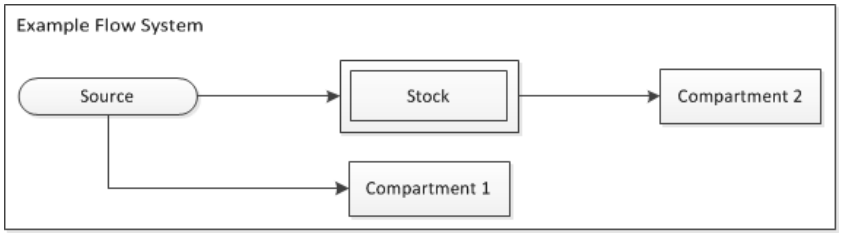

Figure 2.1: Basic Structure of the Example System

For the idealized example we chose the following specific parameterisation:

- **Material Release:** It was assumed that the knowledge about the actual material release is incomplete. We made the assumption of an empirical distribution function. A periodic material release from source of 500 t/y is assumed with the likelihood of 0.2, 100 t/y with a likelihood of 0.5 and 1500 t/y with 0.3. The periodic release is constant and should not be varied between the periods.
- **Flows:** The knowledge about the allocation of the material released from source leads to a normal distribution. Each period 0.6 of the total material released are assumed to be transferred to the "Intermediate stock" with a standard deviation of 0.2. This value is assumed to have a variant behaviour over time. The remaining part of the material is transferred to "Compartment 1".

- **Delayed release from stock:** All material transferred to the "Intermediate Stock" remains there for 2 years. Afterwards the material is transferred to "Compartment 2" with a rate of 0.5 per year. The investigation period of the system is 10 years.

2.3. Implementing the four models of the example system

This section describes the implementation of the models using each of the four modelling approaches. Special attention is paid to the modelling and simulation process and the general procedure, how and to what extent the specific aspects could be implemented and general particularities observed.

2.3.1. System Dynamics using Vensim

The System Dynamics approach assumed continuous (flow) processes. The underlying mathematical model represents these processes as a set of differential equations. To simulate the model the equation system has to be solved for the time instants of interest. In general differential equations are not analytically solvable, which is the reason why numerical methods are applied. For our implementation we chose Runge-Kutta 4 with a basic calculation time step of 0.125 of the basic time unit 1 year. In the first step of the implementation of the example system, we had to define the static model structure. All model components had to be placed and connected on a canvas by drag and drop. First the three compartments of the example system are placed as Levels (stocks). They can change their values constantly over time. Flows among the stocks or between stocks and the system's environment are displayed as uni- or bidirectional Rate pipes. Factors that influence the behavior of material flow amounts and rates were modeled as Auxiliaries. They represent the information flow of the system. Auxiliaries do not keep information between the calculation steps. Dependencies in the model are visually defined as arrows between the model variables.

After the model was composed of its static elements the actual behavior of the components was applied to the model components as mathematical functions. The Levels were set with 0 as initial value, because our example system starts with empty stocks. The change rates of stocked material in the Levels are described as the sum of the inflows rates stock minus the sum of the outflow rates. The values of flow Rates and Auxiliaries are displayed by a single value that is either constant or a function of values of other variables that is determined in each calculation step. During simulation, the calculation

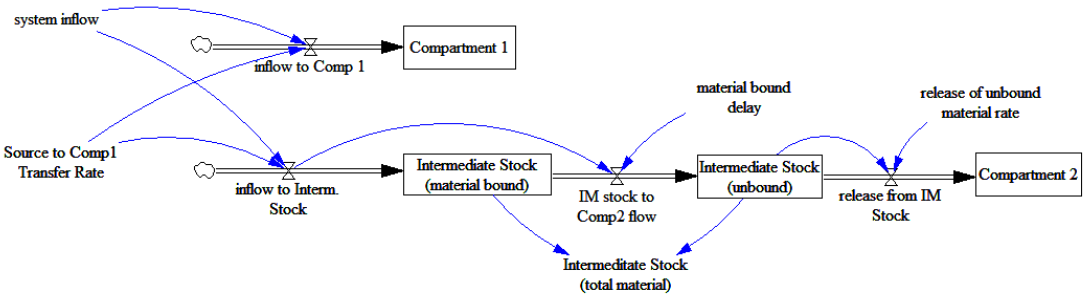

Figure 2.2: Structure of the Vensim Model

steps are iterated, each calculating the periodic flows and then updating the system state.

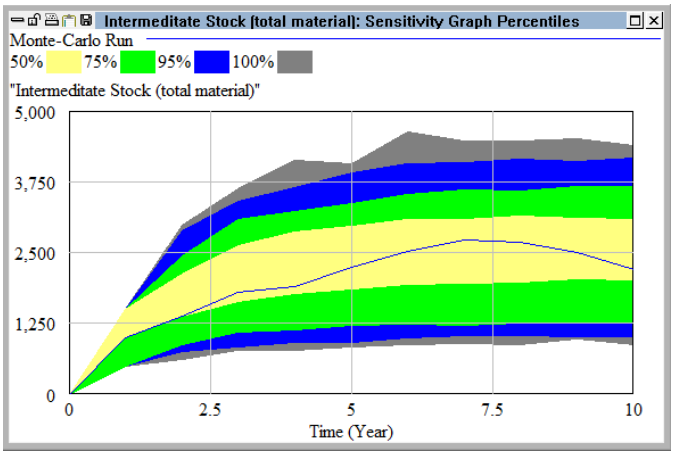

Figure 2.3: Evaluation of material in Intermediate Stock over time

Vensim provides an infrastructure to perform Monte-Carlo simulation to examine model behavior under uncertainty. It allows the modeler to assign probability distributions to model parameters to represent the uncertainty about its true value and evaluate the model behavior over a large set of simulation runs. In our example we varied the system inflow parameter between the simulation runs. To express the empirical probability distribution we first generated a uniform distribution and had to map it in a second step to the specific distribution using a Lookup function. For the transfer coefficient that splits the total system inflow into a flow to Compartment 1 and Intermediate Stock the parameter is varied between all periods. The intermediate stock compartment was implemented by splitting it up into two Level variables. The first one represents the stocked material that is bound for the first two periods. After these periods the material

is transferred to the second Level variable. The flow rate is defined using the inflow to the previous compartment and a fixed delay function. The actual material stored in the intermediate stock compartment is displayed by an Auxiliary that sums up the material from both stocks.

Simulation results can be displayed as tables and diagrams for all model components. Vensim provides functions for data import and export.

2.3.2. Material Flow Networks using Umberto

In Material Flow Networks (MFN) the static structure of a model is a Petri net (for an introduction to Petri nets see Peterson (1981)). It consists of places that hold materials, and transitions that connect two or more places. In MFN, the transitions define material transfers as a transformation rule of inputs to outputs. In particular, they specify all the material types and relative amounts. To implement the example system we first defined the total simulation time period as 10 single periods of one calendar year. Then we modeled Source, Compartment 1, Compartment 2 and the Intermediate Stock as places. In Umberto, places are suitable to account the amounts of stored material and their changes over the whole simulated period. All flows between the compartments were implemented as transitions. In accordance with the Petri-net notation the Source compartment was designed as "source" place and Compartment 1 and 2 as sinks. Flows from one place were aggregated to one transition that holds the actual algorithm of the material transfer. In the case of Transition 1 (Figure 2.4) it comprises the two transfer coefficients of the flows to the two subsequent compartments. Umberto provides a basic support for Monte-Carlo simulation with the most commonly used mathematical distribution functions. So the split flow from the source to compartment 1 and the intermediate stock could in general be assigned with a normal distribution for the transfer coefficients. However, the implementation was not really straightforward because probability distributions cannot be directly assigned to a variable in a transition but have to be declared globally as "net parameter" and then introduced in a second step into the intended model parameter. The implementation of the periodic material release as empirical distribution was not supported by Umberto. Instead a constant value was used. The application of Monte-Carlo simulation in Umberto is limited to a single period. The variance of model parameters is processed only for the current period. To the following period only the average value of the sample is transferred. The time delayed release of material from the intermediate stock compartment could not be implemented as an internal model logic. Umberto was not built to model time dynamic behavior. To

implement the model nonetheless, the release from Intermediate Stock was calculated manually and the flow between Intermediate stock and Compartment 2 parameterized accordingly. The underlying model of a material flow network is a linear equation system which is determined by the transfer rules of the model. Using Monte-Carlo simulation it becomes a probabilistic model. Umberto enables a representation of results as Sankey diagrams for the flows of one period. Results of Monte-Carlo simulation can also be displayed in the form of bar charts.

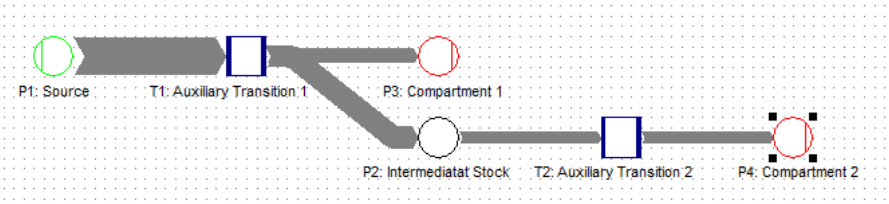

Figure 2.4: Implementation of the Example System using Umberto

2.3.3. Material Flow Analysis using STAN

In MFA a system of dependent flows is represented by a set of processes and the flows of substances and goods between them. System changes over more than one time period are represented as changes in stocked material which is accounted for over the entire simulation time. In the first step of the modelling process we had to determine some global settings. We chose a period length of one year and a total number of 10 periods. A year was also chosen as the temporal reference unit and the finest granularity. In the second step the model structure was defined using a drag and drop interface. The compartments of the example systems were modeled as processes. Compartment 1 and 2 and the Immediate Stock were modeled as stocks. Furthermore, the material flows were defined. There are flows between processes and in- and out-flows over the system border. Finally, the model was parameterized, by assigning specific values for flows and dependencies. We assigned the inflow to the model as Flow 1. The transfer coefficients that split the total inflow to a flow to Compartment 1 and Intermediate Stock are assigned in the Production Process. As Umberto, STAN does not provide means to represent the complex and time delayed release behaviour from the Intermediate Stock. Therefore the time dependent release from the “Intermediate Stock” of the example system could not be defined as part of the model. The amounts were calculated manually and used for parameterizing Flow 4. The underlying mathematical model is a system of linear equations. With the given parameterisation the equation system is determined. STAN

can calculate all remaining model variables as dependent values. In this approach, the representation and processing of uncertainty in terms of Bayesian statistics and Monte-Carlo simulation in not feasible. Instead STAN enables the handling of uncertainty as standard deviation of a normal distribution. It supports the concepts of error propagation and equalization calculus. In the example implementation, uncertainty was modeled using standard uncertainty.

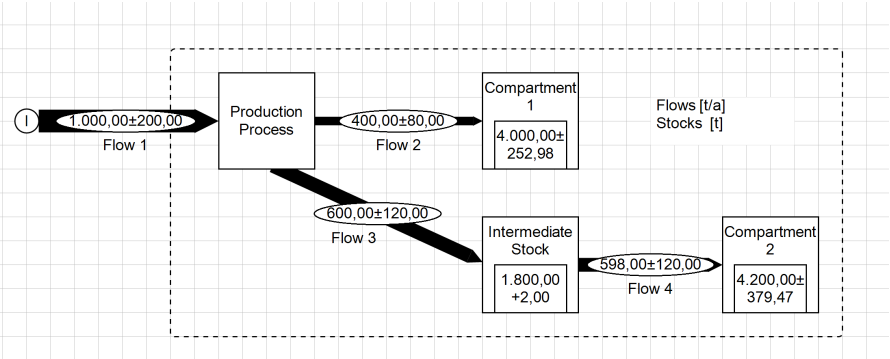

Figure 2.5: Implementation of the Example System using Stan

2.3.4. Probabilistic Material Flow Analysis in R

Probabilistic material flow analysis (PMFA) extends the basic approach of material flow analysis. In PMFA incomplete knowledge is expressed as a set of assumptions with assigned Bayesian probabilities. It allows calculating equilibrium for a set of interacting flows and representing existing uncertainties about the actual values of the original system using Monte-Carlo simulation. The example implementations in system dynamics, material flow networks an MFA were each performed using a specific software tool. Currently, there is no software tool that specifically supports the design and use of PMFA models. The model it is instead implemented in the programming language R. In the first step of the modeling process all dependencies between system variables were transferred into a mathematical equation system (Eq. 2.1), representing the static structure of the system. In a following step, uncertain knowledge is displayed in the model. Bayesian probability distributions are applied considering all knowledge about the system dimensions. In this case we created an empirical probability distribution for the material release from “Source” that regards all assumptions made and their likelihood to be true. The transfer coefficients for the flow between “Source” and “Compartment 1” and “Source” to “Intermediate Stock” are displayed by a normal distribution as given in

the example system. PMFA is not intended to model time dynamic behavior. For this reason the "Intermediate Stock" was not included in the implementation. Instead, the inflowing material is directly transferred to "Compartment 2".

$$\begin{aligned} \delta Comp1 &= totalInput * TC_{InComp1} \\ \delta Comp2 &= totalInput * (1 - TC_{InComp1}) \end{aligned} \tag{2.1}$$

The model behavior is produced using Monte-Carlo simulation. Therefore, a large set of simulation runs is performed and evaluated with statistical methods. In each simulation run the model parameters are set with a random value coming from the assigned probability distribution. Then the equation system of the model is solved to determine the values of all variables.

The use of the programming language R instead of a specialized tool demands a larger previous knowledge from the modeler about the modeling approach and the language R. Also, there is no specific modeling guidance by the tool and no predefined visualization. However, as a language for statistic calculation and visualization, R provides a large range of possibilities to visualize simulation results. Figure 2.6, for instance, displays a plot the simulation results as probability densities, mean values, and quantiles for the stocked material of Compartment 1 and 2. Furthermore, aspects that are not part of the pure PFMA approach can be represented making use of the general features of the language. This also enables an extension of the existing PMFA approach to system aspects that are not included yet such as the change of the system state over time.

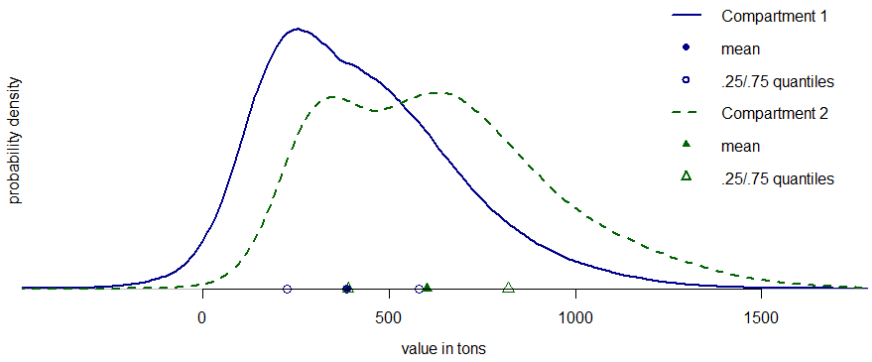

Figure 2.6: Modeling in PMFA (using R), probability densities of stocked material amounts after one period

Criterion	Material flow analysis (STAN)	Material Flow Networks (Umberto)	System Dynamics (Vensim)	Probabilistic Material Flow Analysis (R)
Empirical distribution as model input	-	-	++	+++
Normal distribution for transfer coefficient	+	+	+++	+++
Time delayed release from stock	+	+	+++	+

+++	Modelling possible and well supported
++	Modelling possible, but not supported; not in the focus of the modelling approach
+	Modelling partly possible or only with much effort; not in line with the modelling approach
-	Modelling not possible

Table 2.1: Evaluation of the modelling approaches

2.4. Discussion

The aim of this study was to evaluate the capabilities of existing material flow modelling approaches for assessing environmental concentrations. Therefore, an idealized example system was developed that includes the most crucial issues of environmental flow processes. This example system was implemented using several material flow modelling approaches. The evaluation of each of the implementations of the example system reveals a ranking of the capabilities of each single approach to perform the entire modelling process (see Table 2.1). While classical MFA and material flow networks were not able to model most of the system's aspects, system dynamics and PMFA showed greater capabilities. Altogether, Vensim could implement the example most adequately, closely followed by PMFA.

The approaches differ considerably regarding the way uncertain knowledge is represented and processed. STAN handles uncertainty as standard deviation from a mean value. Thus, uncertainty can be processed by error propagation and equalization calculus. The other approaches represent uncertain knowledge using Bayesian statistics and Monte-Carlo simulation. That way, they enable a more differentiated treatment. Monte-Carlo simulation in Umberto is constrained by some general limitations. It can

only be applied for one time period. The sample that represents a system variable is transferred to the next period as the single average value. Furthermore, the probability distributions have to be defined in a rather complicated way as global "net parameters". In a second step they have to be assigned to the specific model variable. Empirical probability distributions cannot be represented in Umberto. In contrast to that, Vensim and PFMA are able to represent and process all aspects of uncertainty of the example model. However, in Vensim some small limitations occur. At the implementation of the empirical probability distribution for the material release an auxiliary modelling step had to be performed. To emulate the probability function, a uniform distribution had to be mapped onto a lookup function. The representation of a delayed material release from a local stock could be best implemented using Vensim. Since System Dynamics was developed to display dynamic and time dependent system behaviours, this system aspect fits to the scope of the approach. In STAN and Umberto the system behaviour is represented as the change of stocked material. The level of a stock at the end of a time period is transferred to the next period as initial value. The actual model logic is explicitly parameterized for each period, which makes it impossible to deal with a more specific time dependent behaviour. PMFA does not include a method to represent system changes over time. However its implementation using R enables to model a specific system behaviour that exceeds the current specifications of the approach. As a general remark, none of the four approaches was able to represent and simulate the entire example model satisfactorily. In the modelling and simulation process of a real-world case, this will presumably have even stronger consequences on the reliability and significance of the obtained results, because these systems are usually larger in size and complexity than our example system. Therefore, a new approach that combines the advantages of the modelling approaches investigated could be of great value. For the development of this approach it seems reasonable to take PMFA as a starting point and extend it by the stock and flow methodology of System Dynamics. Since PMFA is implemented using the language R it provides a large range of probability distributions to represent uncertainty. To base the new approach on PFMA instead of System Dynamics has the advantage to avoid the inherent discretisation error and additional computational effort of continuous simulation in System Dynamics. Furthermore, the model implementation using the R language leads to a straightforward adjustment and extension of the existing modelling approach.

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3

A Dynamic Probabilistic Material Flow Modeling Method (Paper 2)

Original publication:

A Dynamic Probabilistic Material Flow Modeling Method

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Abstract

Material flow modeling constitutes an important approach to predicting and understanding the flows of materials through the anthroposphere into the environment. The new "Dynamic Probabilistic Material Flow Analysis (DPMFA)" method, combining dynamic material flow modeling with probabilistic modeling, is presented in this paper. Material transfers that lead to particular environmental stocks are represented as systems of mass-balanced flows. The time-dynamic behavior of the system is calculated by adding up the flows over several consecutive periods, considering changes in the inflow to the system and intermediate delays in local stocks. Incomplete parameter knowledge is represented and propagated using Bayesian modeling. The method is implemented as a simulation framework in Python to support experts from different domains in the development of their application models. After the introduction of the method and its implementation, a case study is presented in which the framework is applied to predict the environmental concentrations of carbon nanotubes in Switzerland.

Keywords

material flow modeling, simulation, Bayesian modeling, uncertainty handling, prediction model, environmental modeling, environmental exposure assessment

Software Availability

The simulation framework is available as a software package via PyPI, the Python Package Index at:

https://pypi.python.org/pypi/dpmfa-simulator.

3.1. Introduction

The quantification of the environmental concentration of an anthropogenic pollutant is a crucial step toward the determination of risks for humans and ecosystems emerging from the application of new materials. While direct, quantitative measurements are often not feasible, the representation of material flows that lead to those concentrations provides means for an indirect assessment. The knowledge about these flows is the starting point for multimedia environmental fate models, which regard systems as sets of clearly separated, distinguishable compartments and allow the investigation of material transfers between them (MacLeod et al., 2010). "Multimedia" in this context refers to the fact that multiple environmental media (air, surface water, groundwater, soil) are considered parts of the system under study.

In general, material flow modeling approaches are well suited to investigate a large range of anthropogenic pollutants. For the assessment of the arising environmental stocks, the relevant flow processes need to be investigated. Depending on the pollutant and the scope of the investigation, this may include the material production, the application and use in different products, subsequent waste handling processes, and flows between environmental media. Different scopes of a study can introduce further aspects such as geographical distribution or a more detailed subdivision of (e.g. technical) processes.

Existing mass flow modeling approaches such as material flow analysis (MFA) (Baccini and Brunner, 1991) regard systems of stocks and flows using mass equations to derive dependent system dimensions. They are supported by the software tool Stan (TU Vienna 2012) for general flow modeling purposes and the Umberto software ifu

Hamburg GmbH (2014) for material flows in the domain of corporate environmental management. These programs (STAN and Umberto) also support uncertainty representation and propagation, but are restricted to a set of given distribution functions. They also support a period-based time representation. However, the update of the system state is determined by an explicit definition of the flow model for every period and not based on an underlying set of rules (e.g., for the residence times in stocks).

In environmental modeling, however, often considerable uncertainties exist about the volume of a flow, the rates with which the total amount divides into partial flows, and the particular pathways they take. Available data sources may be based on imprecise, incomplete or even contradictory assumptions. The explicit representation of these uncertainties and their propagation through the model can lead to more meaningful simulation results, thus allowing more reliable predictions of the resulting environmental concentrations. Bayesian modeling provides a technique for representing and propagating incomplete system knowledge and translates uncertainty about the true value of a system variable to the model as a probability distribution for the model parameter in question. It represents the modelers' assumptions about the true value, which can vary both concerning the type and the parameters of the probability distribution. Based on the given distributions, the distributions of the dependent values are then inferred using Monte-Carlo (MC) simulation. Money et al. (2012) proposed a Bayesian network of several stages for forecasting environmental concentrations of nanoparticles.

The probabilistic material flow analysis (PMFA) approach, was developed by Gottschalk and colleagues (Gottschalk et al., 2010a). They built a flow model that includes a complete assessment of uncertainties in all model parameters. It applies Bayesian modeling to propagate incomplete knowledge about the absolute inflow to the system and the internal dependencies between the downstream flows. Over a large sample size, steady states of flows are calculated, each based on a sampled set of random values. From that the resulting absolute material flows are determined. PMFA has mainly been applied for assessing environmental flows of nanomaterials (Gottschalk et al., 2009, 2010a; Gottschalk and Nowack, 2011; Sun et al., 2014).

The simulation of systems over significant periods enables the estimation of absolute stock volumes. This includes, in particular, systems with time-dependent inflows and residence times in stocks. To represent time-dependent residence times, dynamic models become necessary because the release of one period depends on the inflows of several previous periods and the delay characteristic of the stock. Such models partially include dynamic system behaviors, such as the scaling of a flow of a reference year to estimate annual flows for previous periods and add up those inflows to a stock to obtain absolute

volumes (Gottschalk et al., 2009) or the calculation of flows over subsequent periods based on clocked releases defining rates from the absolute stock of a well-mixed reactor (Walser and Gottschalk, 2014). These models provide a probabilistic material flow representation and a limited representation of changes over time. However, time-dependent external material inflows and material release from stocks as functions with varying residence times and release rates are not included. Moreover, in the studies mentioned above, special-purpose models were developed for particular cases. These studies do not provide a general method of how to model systems of this type, nor do they provide a conceptual and operational framework to support the modeling and evaluation process.

Outside the field of probabilistic modeling, many material flow modeling methods are in use that provide means to represent dynamic system behavior over time. Müller et al. (2014) present a survey on a large range of these methods, focusing on the uncertainty handling of these methods. While a large share of the methods do not consider uncertainty at all (>50 %), there are some that use sensitivity analysis (37 %), Gaussian error propagation (6 %) or parameter ranges (5 %), but none supports full Bayesian uncertainty representation and propagation.

Dynamic Bayesian networks that are mainly used to learn and reproduce time-dependent system behavior (Daly et al., 2011) process uncertain knowledge in a time-dynamic model. However, this approach focuses on variances in state transitions and does not include flow-specific behavior.

To summarize, what is missing is a method for investigating the development of environmental stocks of a pollutant by building a model which satisfies the following requirements:

- It represents a system of mass balanced dependent flows,
- it considers changing material releases and intermediate delays in local stocks over a significant time horizon, and
- it provides means to represent and process incomplete parameter knowledge.

In (Bornhöft et al., 2013) we investigated several existing methods regarding their capabilities for meeting these requirements in more detail and revealed that no existing method fulfills these requirements.

In the present article, we present a modeling approach that merges the advantages of the existing techniques of probabilistic material flow modeling with the existing approaches to dynamic material flow modeling. The combined method forms the basis for a software framework that supports the development, implementation, and simulation of

dynamic probabilistic material flow models. We will describe how we implemented this framework as a software package using the Python language (Python Software Foundation, 2014) to support experts in building specific models in their field of application.

Finally, we will demonstrate the application of the framework using a realistic case study. This case includes the implementation of a model to investigate the system of flows of engineered Carbon Nanotubes (CNT) in Switzerland. Due to their toxic properties to humans and ecosystems, CNTs pose potential risks (Savolainen et al., 2010). Sun et al. (2014) presented a steady-state model to assess the inflows to different environmental compartments based on data for the year 2012. However, CNTs are very stable and accumulate in the environment over time. Moreover, they are usually applied in products with long lifetimes, which leads to significant material amounts bound in use-stocks. A dynamic model is therefore needed to provide a more detailed and adequate system representation. Based on this example application, the new approach is discussed in more detail regarding general functionality and its opportunities and limitations.

3.2. Description of the method

We propose a new method that combines the advantages of the existing approaches to probabilistic and dynamic material flow modeling: dynamic probabilistic material flow analysis (DPMFA). It aims to close the gap in existing techniques for exposure assessment by providing means to model and simulate systems of complex, dependent material flows, consider the dynamic behavior of the system over time, and explicitly represent and propagate incomplete parameter knowledge. For that purpose, a set of components is provided as building blocks for the model. These components need to be instantiated and linked together to represent the investigated system, and to allow simulation and evaluation.

We first outline the main idea of the approach, describing the basic structure of the models, the simulation processes and how the elements of the previously introduced modeling methods are combined. The implementation of the framework as a software package in Python is described on that basis in a second step.

Each DPMFA model is an abstraction and idealization of an original system of flows in the technosphere and the ecosphere. The model is reduced to the parts and aspects that determine the behavior investigated. Following the scope of the simulation study, the system is first subdivided into a set of compartments. They constitute the static model structure and structure the system into spatially or logically separated units (e.g., as in

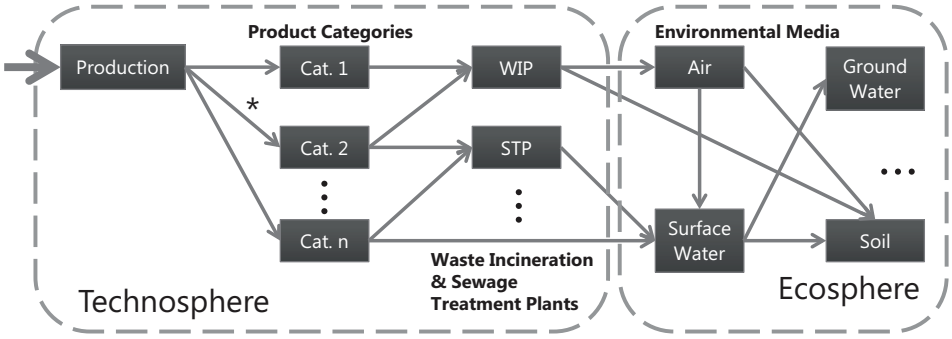

Figure 3.1: Pathways of material flows of anthropogenic pollutants from the technosphere via different product categories, waste incineration and sewage treatment plants to the ecosphere. Specific system compartments and flow dependencies need to be implemented for each particular material and scope.

Figure 3.1). The actual breakdown depends on the objective and the scope of the study. All material inflows, transfers, accumulations, and releases refer to these compartments.

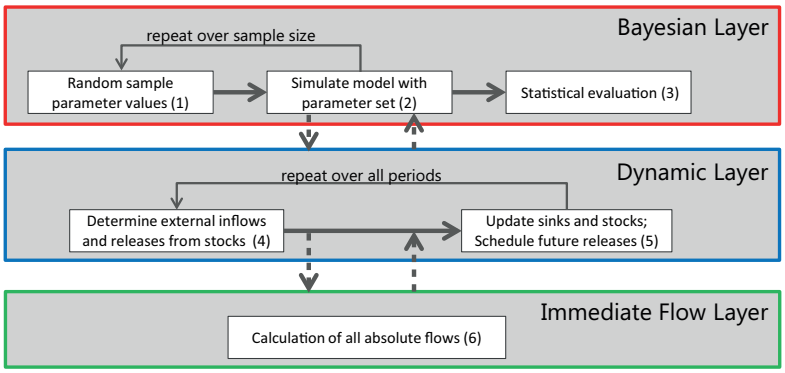

Figure 3.2: Dynamic Probabilistic Material Flow Analysis — structure of the simulation process

Simulation experiments need to be performed with the model to assess material stocks and flows over time. Based on the results of these experiments, conclusions about the processes of the original system are drawn. The general simulation mechanism for investigating the flows between the compartments is structured as a 3-layer process (see Figure 3.2). On the first – the Bayesian – layer, parameter uncertainty about the flow dependencies between the system compartments and the absolute annual inflow is represented by Bayesian probability distributions. These uncertainties are then propagated through the model for the entire simulation time using Monte-Carlo techniques.

The second layer refers to the time-dynamic model behavior. Time is represented as a

sequence of successive periods (usually years). For each period within the time horizon of the simulation, the external inflows to the model, the material accumulation in stocks, and their local material releases are determined and added up.

To enable this, the third layer provides a mechanism that calculates the absolute material flows for a period based on absolute material releases and the flow matrix, taking all transfer dependencies into account.

3.2.1. Static structure

The static model structure consists of a set of persistent entities. They represent the local relations of the compartments and are assembled to derive the global system behavior. The basic model components are flow, stock, and sink compartments and external inflows.

- A flow compartment includes material inflows and relative outflows of a delimited spatial of logical system area.
- A stock compartment is a component with a temporary total or partial material accumulation and later re-release of the material. Stock compartments include local material in- and outflows and provide a delay function that determines material accumulations and releases.
- A sink compartment is a component with permanent material accumulations.
- An external inflow is a source that implies a time-dependent exogenous input to a stock or flow compartment (e.g., through production or import).

The dynamic model behavior emerges from the interplay of these static components over time.

Material flows

The calculation of absolute values for the material transfers is derived from existing material flow analysis approaches using a classical Leontief model (Leontief, 1986). It represents the material flows of one period as immediate and simultaneous. While exogenous inflows to the system are defined as absolute material inflow values to a compartment, endogenous flows from a compartment are defined by transfer coefficients (TC). The transfer coefficient TC_{js} defines the relative mass flow m from compartment j to s as a proportion of the sum of all inflows to compartment j (Eq. 3.1).

$$TC_{js} = \frac{m_{js}}{\Sigma_r \; m_{rj}} \tag{3.1}$$

To determine the absolute flows of the model, all transfer coefficients are assembled to the flow matrix A (Eq. 3.2).

$$A = \begin{array}{c|ccc|ccc} & C_1 & ... & C_m & C_{m+1} & ... & C_n \\ \hline C_1 & 1 & ... & -TC_{m,1} & 0 & 0 & 0 \\ ... & ... & 1 & ... & 0 & 0 & 0 \\ C_m & -TC_{1,m} & ... & 1 & 0 & 0 & 0 \\ \hline C_{m+1} & -TC_{1,m+1} & ... & -TC_{m,m+1} & 1 & 0 & 0 \\ ... & ... & ... & ... & 0 & 1 & 0 \\ C_n & -TC_{1,n} & ... & -TC_{m,n} & 0 & 0 & 1 \end{array} \tag{3.2}$$

The flow rates from one compartment to another are read diagonally from top to left. The compartments C_1 to C_m represent immediate flow dependencies, compartments C_{m+1} to C_n sinks. The absolute material inflows to the system are expressed as an input vector I (Eq. 3.3).

$$I = \begin{pmatrix} g_1 \\ g_2 \\ . \\ . \\ g_n \end{pmatrix} \tag{3.3}$$

The vector comprises the sum of the current external inflows and the releases from the model stocks to all compartments C_1 to C_n as elements g_1 to g_n. Solving the System (Eq. 3.4) for an unknown column vector X leads to a steady state of flows.

$$AX = I \tag{3.4}$$

The column vector X determines the inflows to the compartments with which the stocks are incremented. If the sum of each column of a flow compartment in the coefficient matrix is zero and the entire inflow is allocated to the sink columns as a non-zero value, the system is mass-balanced. All material inflows are distributed to the sinks based on the relative local flow dependencies.

Flow Compartments

In the model, the relative transfer dependencies are bound to flow compartments, which represent points in the system where material flows are gathered and split up. Several transfers can be bound to one flow compartment. Each transfer includes a target compartment and a transfer coefficient. The combination of all outgoing transfer coefficients from a compartment enables to ensure a mass-balanced system. Therefore, the outgoing transfers from each compartment need to sum up to 1 to create a global balance. To assemble the flow matrix (Figure 3.3) the outgoing TCs from the flow compartments are transformed into the columns of the matrix.

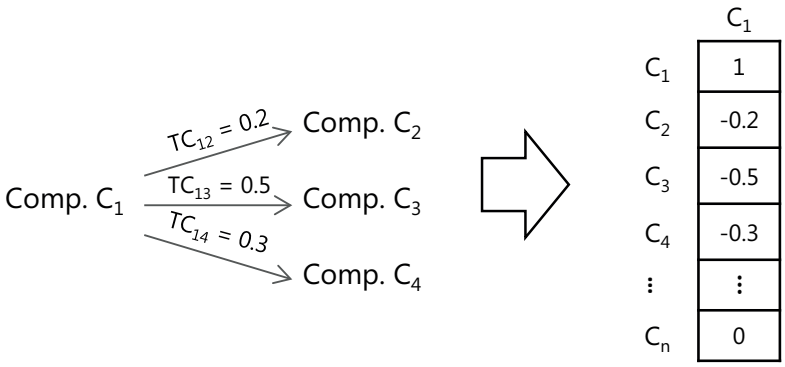

Figure 3.3: : Outgoing TCs from Compartment 1. The set of TCs corresponds to the respective column of the flow matrix (Eq. 3.2).

3.2.2. Time-dynamic behavior

Time advancement is represented in the model as a series of subsequent periods T_0 to T_n of equal length. In each period, the model-wide material flows are determined and used to update the stocks and sinks:

- First, the external inflows and the material releases from stocks are determined (Figure 3.2, Box 4).
- Second, the flows of the period are determined based on the inflows and releases (Figure 3.2, Box 6) by assigning the respective material inflows to the input vector I (Eq. 3.3) and by solving the flow matrix of the system (Eq. 3.4).
- Finally, the stocks and sinks are incremented with their particular inflows from the solution vector X (Figure 3.2, Box 5).

Once the model is simulated over the required time interval the total material in a sink at the end of this interval can be predicted.

External Inflows

Material inflows from an external source to a system compartment are defined as absolute material inputs for a particular system compartment and period. A time dynamic development of these inflows is either represented by a list defining an input volume for each period or as a function of time over all periods. The particular inflow of a period to a particular model compartment C_i is added to the inflow vector I at the element g_i.

Stock compartments

Stock compartments represent material flows through system areas, where at least a part of the material transfer is not immediate.

Therefore, the stock compartments include:

- A set of transfer coefficients that determine the proportions of the material leaving the compartment to particular subsequent compartments; this is analogous to the Flow Compartments (Figure 3.3). However, due to residence times >0 of the material in stock, the periodic outflow to a stock compartment does not match its inflow. For a consistent definition of the relative proportions of the outgoing flows, the TCs are here defined as the relative ratio to the total outflow of a stock compartment.

- A release function $releaseFct(t)$ that defines relative times and proportions for the materials (re-) release based on the time of the material inflow t_0.

The release function defines the residence times and the rates with which materials that enter the stock compartment are released again. For the calculation, the immediate release in period 0 and those in later periods are treated in different ways. The portion immediately released is included to the flow matrix A. Therefore, the outgoing TCs from the stock are multiplied with the immediate release rate $releaseFkt(t_0)$ and added to the flow matrix as column, in just the same way as the TCs from the flow compartments. The portion of the material that is released with some delay is treated as described below.

To determine the dynamic development of the stored amounts in stock and the time-dependent material releases, a stock compartment includes the following elements:

- An *Inventory* displaying the current, absolute stocked amounts. To enable the evaluation of the stocked values, the inventory is modeled as a list, recording the stock for all periods.
- A *ReleaseList* that includes the scheduled material releases for the future periods

During the calculation of the flows of period i, the following steps are performed in stock compartment.

I. At the beginning of the period T_i:

a) Transfer the stocked amount from the previous period to the current period as the initial value (Eq. 3.5). (This step is omitted in the first period):

$$Inventory(T_i) = Inventory(T_{(i-1)}) \tag{3.5}$$

b) Determine the total release from the stock for the period (Eq. 3.6) and reduce the inventory by that value (Eq. 3.7):

$$currentRelease = ReleaseList(T_i) \tag{3.6}$$

$$Inventory(T_i) = Inventory(T_i) - currentRelease \tag{3.7}$$

c) For **each** outgoing TC_{js} from stock compartment j, include the portion of the current release to the inflow vector I (Eq. 3.8):

$$I(g_s) = I(g_s) + currentRelease * TC_{js} \tag{3.8}$$

II. After calculation of the global flows (Figure 3.2, Box 6) the stock compartment is updated with the respective material inflow from the solution vector X:

a) Add the not-immediately released portion to the inventory (Eq. 3.9):

$$Inventory(T_i) = Inventory(T_i) + X(s) * (1 - releaseFct(t_0)) \tag{3.9}$$

b) Schedule the material releases for the **future** periods (Eq. 3.10):

$$\begin{aligned} &\textbf{For each } k \textbf{ from } 1 \textbf{ to } m: \\ &\quad \textbf{if } i + k \leq n: \\ &\qquad ReleaseList(T_{(i+k)}) = ReleaseList(T_{(i+k)}) + X(s) * releaseFct(k) \end{aligned} \tag{3.10}$$

Uncertainty representation and processing

In exposure assessment modeling, incomplete knowledge may concern the point in time, the location or the extent of a flow. This uncertainty is mainly epistemic, which means it relates to a general lack of knowledge about the true value of a system variable. Such uncertain variables are represented using (Bayesian) likelihood distributions, which include all plausible values and assign normalized probability densities. The dependent system variables (e.g. a stock at a particular time) are calculated using Monte-Carlo simulation, i.e., the model is repeatedly evaluated over a large sample size m. For each single run $i \in m$, all uncertain parameters are assigned a random number from the associated parameter distributions (Figure 3.2, Box 1). With this parameter setting, the model is calculated over all periods as described above (Figure 3.2, Box 2). As a result, the dependent model variables (e.g. stocks) are available as an $m \times n$ matrix. Based on that representation, statistical evaluations and visualizations can be performed (Figure 3.2, Box 3).

The parameter distributions are either regarded as parametric distribution functions or as non-parametric distributions. Depending on the origin of the available data, there may by samples from direct observations, results of previous simulation steps, or probability distribution functions representing the assumed characteristics of the distribution. Since it is possible to sample random values from either variant for the Monte-Carlo simulation, both are suitable for representing uncertain knowledge about absolute inflows and transfer coefficient in the model.

The representation of uncertainty in transfer coefficients and external inflows has some important characteristics. For modeling TCs the mass balance of the system needs to be preserved. While in a deterministic mass balanced flow model the sum of the outgoing TCs from one flow compartment or stock have to sum up to 1, in the probabilistic case the marginal distributions for the model parameters have to be chosen in such a way that their *expected values* sum up to 1.

Moreover, in the simulation process, the dependent random values are adjusted after sampling to avoid combinations violating mass balance constraints. The modeler can chose to do so either by a normalization factor over all involved TCs or – in the case of transfer coefficients from underlying information of strongly differing reliability – by defining an order of priority to first adjust the parameter values based on the least reliable data.

The external inflow to a particular compartment over time can be represented either as a list of single probability distributions for each period or by one marginal distribution

representing an uncertain base value and a deterministic growth function. The two variants imply different underlying assumptions. The use of a common base value for all periods emphasizes the inter-periodic dependencies while the absolute value is not exactly known. Expressed as a list of single inflows, the random samples for the periods are assumed to be independent. They implicitly show variant behavior and increasing degrees of freedom of the model with the number of simulated periods and thus a growth of the complexity of model behavior for longer time spans.

3.3. Implementation of the method

Based on the DPMFA method a software framework was developed to support the design and use (i.e., the simulation) of dynamic probabilistic material flow models. It is designed as a Python (2014) package and utilizes the *SciPy* library (Jones et al., 2001) for statistical computation and in particular the `NumPy` package (van der Walt et al., 2011) for matrix representation and calculation.

The program package implements the principle of separation of model and experiment (Page and Kreutzer, 2005). At its core, it provides the infrastructure to perform simulation experiments using the `Simulator` class. This class is provided as a black-box component and is used unchanged by a modeler working with the package. The modeler implements the system-specific logic by assembling predefined components. These are provided as white-box components that the modeler has to adapt to fit the particular behavior of the system under study.

3.3.1. Simulator

The Simulator performs experiments to generate and evaluate the `Model` behavior. As part of the simulation process – as described by our overall simulation algorithm above (Fig. 3.2) – the model parameters specified under uncertainty are assigned random values from the underlying Bayesian probability distributions. Statistical evaluations of the observations over sufficiently large sample sizes approximate the distribution of the variables under the assumptions of the marginal distributions. For each of these parameter sets, the model is simulated over the total investigated time span.

In an iteration over all periods, the `Simulator` determines the external inflows to the system and the local inflows from the stocks. These flows are then distributed to the different model compartments by solving the flow matrix of the model – which is assembled from the internal flow dependencies – with the current inflow vector. Based

on the inflows, the model stocks and sinks are updated. During the experiment, the `Simulator` keeps track of the values of model variables (e.g., the amount of material in a stock).

All of these values are logged in form of a matrix over all samples and periodic values for later statistical evaluation. To facilitate an aggregated evaluation, categories can be assigned to the model compartments. After a simulation experiment is executed, the `Simulator` provides several functions for a category-based evaluation, e.g., to provide total material inflow or outflow or the total material stocked.

3.3.2. Model

The model builder implements a specific simulation model by customizing and combining basic model components:

- Model `Compartment`s representing system entities, which all material flows, accumulations, and releases are related to,
- `Transfer`s defining the internal, relative flow dependencies,
- `LocalRelease`s defining the residence times of materials from `Stock`s and the release rates, and
- `ExternalInflow`s representing exogenous inputs to the system.

An overview of the model structure is shown in Figure 3.4 as a class diagram. The diagram illustrates the model composition and the hierarchy of the included component types. The `Compartment`s are specified by subclasses. `FlowCompartment`s are branches of a flow within one period; `Sink`s mark the material accumulation at an endpoint of a flow process, and `Stock`s represent material flows that are delayed for a particular period of time and later transferred further.

Different `Transfer` types are used to model flow dependencies as relative transfer coefficients to particular subsequent target `Compartment`s.
`ConstTransfer`s define deterministic values as transfer coefficients.
`StochasticTransfer`, `RandomChoiceTransfer`, and `AggregatedTransfer` use probability distributions to represent incomplete knowledge about the true values of transfer coefficients. Random values are sampled for those Transfers during the simulation process.
`StochasticTransfer`s are parameterized with probability distribution functions and respective parameter lists. `RandomChoiceTransfer`s hold lists of values to randomly

draw from. `AggregatedTransfer`s allow weighted combinations of the previously stated `Transfer`s.

All transfers are bound to sources, which can either be `FlowCompartment`s or `Stock`s. To ensure the mass balance of the system, the local transfer coefficients for the relative outflows from such a source have to sum up to 1. This adjustment step is performed after the random values are sampled from the underlying probability distributions. The modeler can either chose to apply a normalization of the corresponding transfers or to define a prioritization to adjust the random numbers from the least credible underlying data. Combinations of both approaches are feasible as well.

`Stock`s represent delayed flow processes. The model builder defines their particular release times and rates as `LocalRelease` strategies. The target compartments and the relative transfer coefficients are defined as `Transfer` objects the same way as for `FlowCompartment`s. To implement LocalReleases, their subclasses need to be implemented. FixedRateRelease defines constant rates for all following periods, `ListRelease` an explicit list of all future release rates, and `FunctionRelease` gives a mathematical function for the particular rates and periods.

`ExternalInflow`s are implemented as `ExternalListInflow` to define explicit inflow amounts for each period or as `ExternalFunctionInflow` with a (growth) function on a base value. To define the base value or the individual values for the list, the model builder has to define `SinglePeriodInflow`s. These can be either deterministic `FixedValueInflow`s or a probability distribution function, namely `StochasticInflow` or `RandomChoiceInflow` from a given sample.

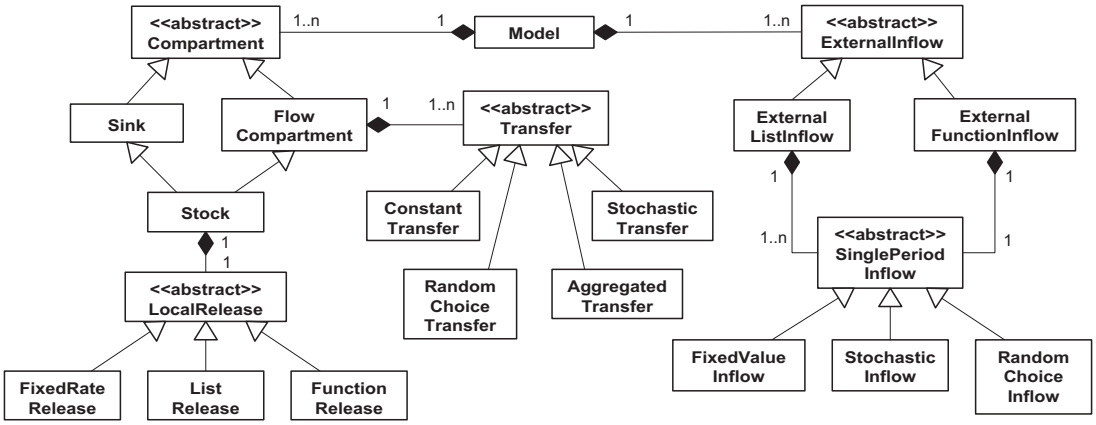

Figure 3.4: UML diagram; composition of the DPMFA model structure

3.4. Example application of the method

The capabilities of the DPMFA method and the corresponding Python package are illustrated by applying them to a case study of practical relevance. Here, we modeled the flows of carbon nanotubes (CNT) in Switzerland to predict current and future material stocks in the technosphere and the environment. CNTs appear to be a useful and challenging example application because of their stability and toxicological properties as well as a lack of analytical methods for a direct measurement of environmental concentrations (Wick et al., 2011). CNT technology is relatively new, and there is a strong increase in current and expected production volumes. Moreover, a large proportion of the produced material is used in long-lasting applications such as polymer composites, which leads to the development of significant use stocks.

The CNT flows were previously modeled using MFA (Mueller and Nowack, 2008) and PMFA (Gottschalk et al., 2009; Sun et al., 2014). The investigated flows include the production of the CNTs, their application in different product categories, their release during the life cycles of the products to technical and environmental system compartments, and the subsequent environmental fate, namely their final accumulation as a pollutant.

The model was simulated on a standard laptop[1] with an Intel i5-4200U CPU @1.6 GHz processor and 8 Gb memory.

3.4.1. The static case

The basic structure of the model, as shown in Figure 3.5, is derived from a steady-state model that we developed earlier to predict CNT flows in Switzerland (Sun et al., 2014). This model includes 31 compartments and sinks and 80 transfers, where all TCs are modeled using parameter distributions. Figure 3.6 exemplarily shows the sewage treatment efficiency as one of those distributions. This distribution determines the proportion of CNTs from waste water that are bound to Sewage Treatment Plant (STP) sludge. The distribution is the result of combining several sources of uncertain evidence. It supports a range of values between 0 and 100 % with a high likelihood of between 82 % and 97 %.

In Sun et al. (2014) the model was originally implemented as a special-purpose application using the R programming language. From that work, we adopted the subdivision of the system into particular compartments and the probability distribution functions that define the transfer coefficients of the flow dependencies between the compartments.

[1] HP EliteBook 840 G1

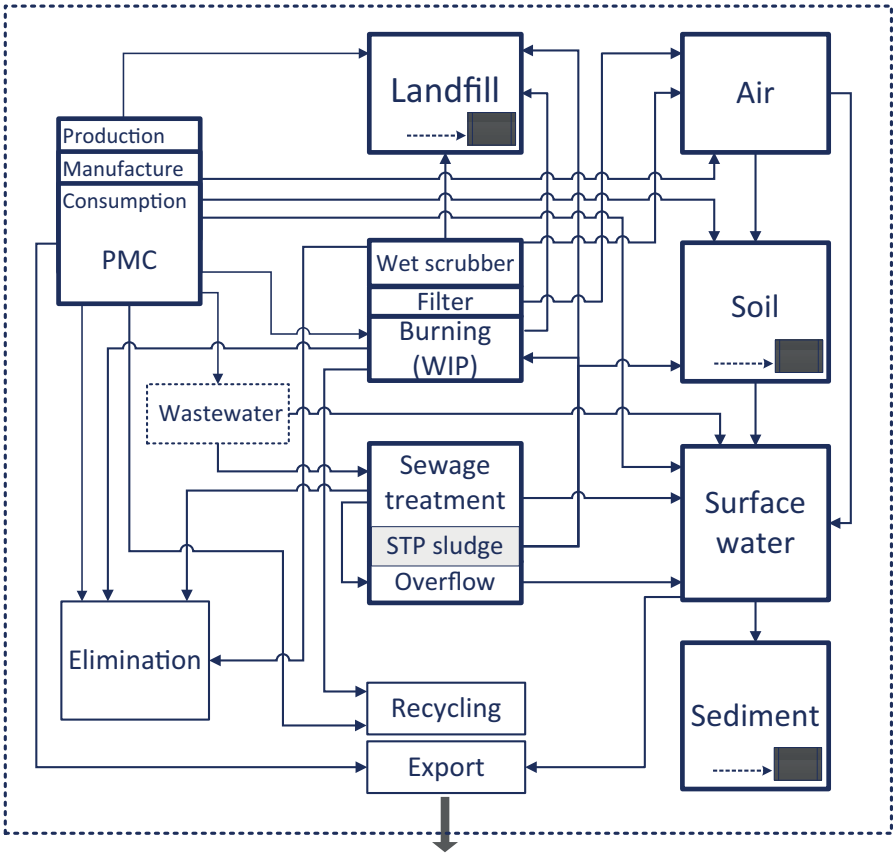

Figure 3.5: Simplified pathways of CNTs to the environment. CNT production, distribution to different product categories and category-specific release are pooled in PMC. Technical waste and waste water treatment processes are pooled as well.

This static model will now be re-built and extended to a dynamic model to demonstrate our new approach.

We first re-implemented the static model using our approach to cross-check the consistency between the two approaches for the static case. To facilitate the cross-check, we created a deterministic version of the model by replacing the parameter distributions with their expectation values and then implemented the deterministic version both in R (as the original model of Sun et al. (2014)) and in Python using the new package. With that, it was possible to compare the basic functionality of the flow calculations of the two implementations.

Then we re-implemented the stochastic version of the original model of Sun et al. (2014) using the new Python package as well. The purpose was to check the influence of

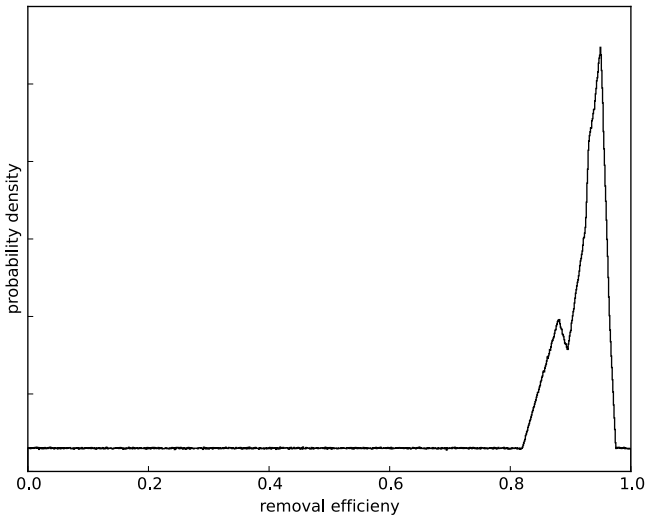

Figure 3.6: Likelihood function of the CNT removal efficiency in sewage treatment plants (STP)

the randomness of the underlying probability distributions on the simulation results. For the stochastic version, we used the same probability distributions as Sun et al. (2014) did. We simulated 50'000 runs which was considered a sufficient sample size. (See the Discussion and Outlook section for a discussion of sample sizes.)

Table 3.1 shows the material inflows to the model sinks as simulation results; in columns 1 and 2 for the deterministic versions of the model in R and using the new Python package, respectively, and in column 3 for the probabilistic version.

The agreement between the simulation results was high. Small discrepancies between the two deterministic implementations can be explained by small numerical errors caused by differences in the underlying algorithms, i.e., for solving the flow matrix, or in number representation. But all in all, the two implementations can be seen as almost equivalent. Differences between the deterministic and the probabilistic model can be explained by the stochastic error, introduced by the randomness of the probabilistic model, which is small due to the large sample size.

In previous works by Gottschalk et al. (2009; 2010a; 2011) and Sun et al. (2014), we focused on the mode value to represent a sample by its most probable single value. Here we mainly use the mean value of the sample. This has some advantages because the mean values show a system of balanced flows. Also, mean values are more robust, especially on small and scattered samples. The computation of a "real" mode value

can be performed only for a discrete set of different values. For continuous variables, the maximum of a density function of the sample, such as the Gaussian kernel density estimator (Scott, 1992), are often used instead.

Depending on the used estimator and its parameters, different maximum values are chosen. However, both the mean value and the mode value represent only a single aspect of a probability sample (Figure 3.7). For more comprehensive insights, the sample itself or at least several dimensions of it have to be considered.

	Deterministic model based on Sun et al. (2014), implemented in R	Deterministic model, implemented using the new simulation package	Probabilistic model implemented using the new simulation package (mean values)
Elimination	7.83	7.82	7.82
Landfill	0.96	0.96	0.97
Soil	0.14	0.15	0.15
Sediment	0.03	0.03	0.03
Cement Plant	0.01	0.01	0.01
Recycling	3.10	3.10	3.08
Export	0.87	0.86	0.87
Sum	12.94	12.94	12.93

Table 3.1: Simulation results – model sinks in tons of CNT/year: Comparison of the mean values of the inflows to the model sinks for 2012. The left column shows the results of the deterministic model in R, using the expectation values of the parameter distributions from Sun et al. (2014). The middle column shows the results of the same deterministic model implemented using the new package. The right column shows the simulation outcome of the probabilistic version of the model implemented with the new package (mean values).

3.4.2. The dynamic case

We extended the static model to a dynamic one by applying historical production volumes as model inflows for previous periods and projections for future periods. This extension demonstrates the advantage of the DPMFA package. It enables the assessment of the absolute material amount in a stock from the sum of the preceding material flows.

The modeled time span begins in 2003 to cover the significant time period in which CNT have been applied on the industrial scale. The annual production volumes are

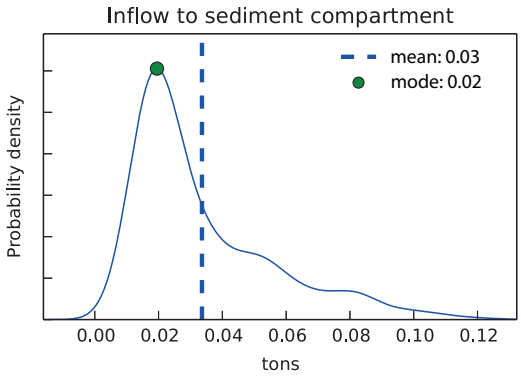

Figure 3.7: CNT inflow to Sediment compartment in the static model: Density function, Mode and Mean value of the sample

derived from Sun et al. (2014) and Piccinno et al. (2012). Missing values for past and future periods are estimated using a quadratic regression function (Figure 3.8). To represent uncertainty about the true production volumes, a standard deviation (SD) is assumed that complies with the relative SD in the sample of the system input from the Sun data. This is implemented as `ExternalListInflow` of single `StochasticInflows` using normal distributions with a respective parametrization.

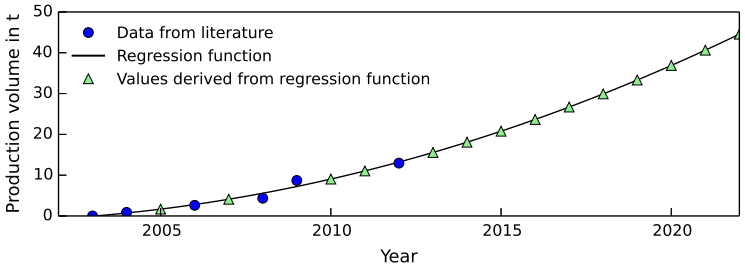

Figure 3.8: Annual production volumes in tons/y; the value for 2012 is taken from Sun et al. (2014), previous years from the survey by Piccinno et al. (2012). Future and missing values were estimated using a quadratic regression function.

CNTs applied in some products have a considerable residence time. This constitutes material stocks with releases after a delay period. Polymer composites, consumer electronics, and automotive have been identified as product categories forming significant intermediate stocks of CNTs (Sun et al., 2014). The delay period of consumer electronics is approximated by a list of relative circulation times of computer notebooks (Stiftung Entsorgung Schweiz et al. 2014) as `ListRelease`. The mean circulation time in the automotive industry is modeled as a normal distribution with a mean of 11.9

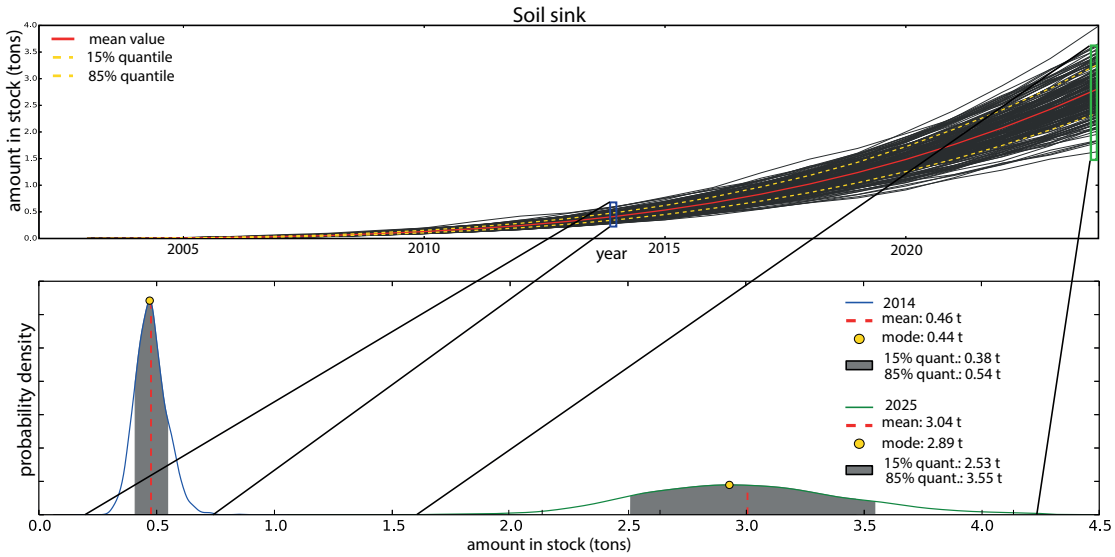

Figure 3.9: Amount of CNT in Soil over time; each grey curve represents a random set of parameter values (a). For the years 2014 and 2025 the sample is projected to a density function (b).

years (Kraftfahrt Bundesamt, 2003) and a standard deviation of 5 years. For polymer composites, a mean delay of 7 years is assumed and approximated by a normal distribution with a mean of 7 and an SD of 3 years. The material releases from both stocks are modeled using a `FunctionRelease`.

3.4.3. Simulation results

The dynamic model was investigated for the period from 2003 to 2025 to predict its material stocks and flows over time. The environmental concentrations of CNTs in soil were determined for the years 2014 and 2025 as examples. Afterward, a second scenario was simulated to investigate the assumption of an immediate production stop of CNTs from 2015 on. Both scenarios were run over a sample size of 50,000 simulation runs. The computation of each took approximately 8:30 minutes. In the first scenario, growing production volumes (Figure 3.8) were assumed.

The change in the amount in CNTs in the soil compartment over time is shown in Figure 3.9a. Each individual curve represents the progress of the material amount in the compartment for one random set of parameter values from the underlying probability distributions, so areas of a high density of curves indicate values with a high likelihood. In the diagram, the number of curves was limited to 500 to increase the clarity of the

representation. However, the mean values and quantiles stated still refer to the full sample. For the years 2014 and 2025, each of the samples of CNTs accumulated in the soil compartment were projected to a density distribution, from which mean and mode values as well as quantiles were derived (Figure 3.9b). Based on the mean values and the significant mass of natural and urban soil of 6.25E+12 kg in Switzerland (Sun et al., 2014), the predicted environmental concentration in soil is 74 ng/kg for 2014 and 486 ng/kg for 2025.

	2012	2014	2025	
			Growing Prod.	Stopped Prod.
Polymer composites	30.60	46.47	172.72	5.09
Consumer electronics	4.00	6.08	22.86	0.96
Automotive	1.87	2.95	12.84	1.78
Sum	36.47	55.50	208.42	7.83

Table 3.2: Mean values (in tons) of the samples of CNTs bound in the technosphere in different product categories, predicted values for 2012 and 2014, and prognoses for 2025 using the assumption of growing production volumes or of an immediate production stop in 2015.

	2012	2014	2025	
			Growing Prod.	Stopped Prod.
Elimination	5.14	10.74	109.49	61.11
Landfill	1.47	2.59	18.19	7.63
Soil	0.27	0.46	3.04	1.20
Sediment	0.13	0.22	1.11	0.29
Cement plant	0.05	0.07	0.37	0.09
Recycling	9.51	15.57	84.64	24.79
Export	2.34	3.86	21.75	6.80
Sum	18.91	33.51	238.59	101.91

Table 3.3: Mean material amounts in sinks in tons, predicted values for 2012 and 2014 and prognoses for 2025 using the assumption of growing production volumes or of an immediate production stop in 2015.

Besides the growth of the amount of material stocked (and with it the environmental concentration), the uncertainty about the true values increases over time as well. While for 2014 the range between the 15% and the 85% quantile is approximately 0.16 tons, for 2025 it is 1.02 tons. The distribution of the CNTs among the different stocks for the years 2012 and 2014 is presented as mean values of the respective samples in Tables 3.2 and 3.3 (columns 1 and 2).

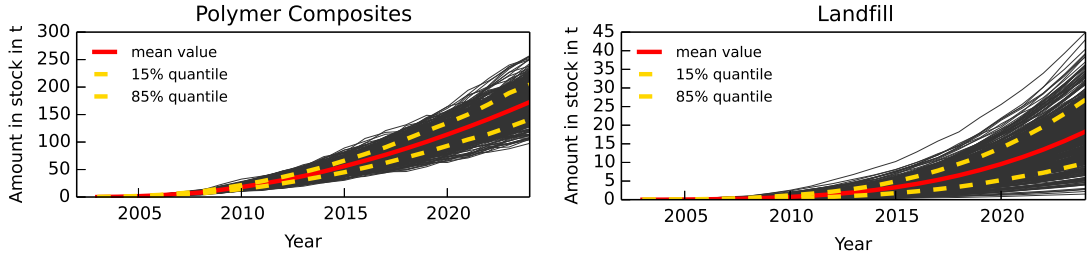

Figure 3.10: Growth Scenario – CNTs bound in products containing polymer composites as stock of the technosphere (a) and in the landfills (b) over time.

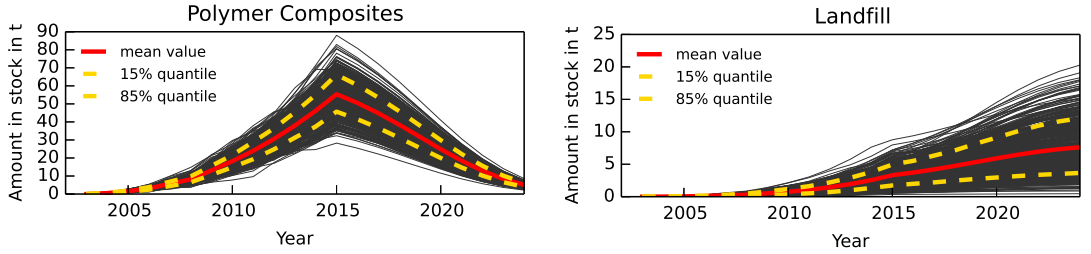

Figure 3.11: Production stop in 2015 scenario – CNTs bound in products containing polymer composites as stock of the technosphere (a) and in the landfills (b) over time.

Table 3.2 shows the in-use stocks of CNTs for the years 2012 and 2014 and for both scenarios in 2025. Table 3.3 shows the accumulated amounts for the model sinks of the technosphere and environmental media. Currently, a large part of the material is still bound in products (in-use stock) – 36.47t (2012), 55.50t (2014) – while only 18.91t (2012) and 33.51t (2014) have been further transferred. This means that in 2012 a share of 65.85% (62.35% in 2014) of the mass that entered the system has not yet been released to the environment. The material that is released from the product categories leaves the system to a large extent via export (3.86t) and recycling (15.57t). Waste incineration and sewage treatment eliminate 10.74t, and subsequently, 2.59t are bound in landfills. The release to the environment has resulted in an amount of 0.46t in soils and 0.22t in sediments (2014) so far. The progress of the stocked material in “polymer composites” as a compartment of the technosphere and in “landfill” as a model sink are pictured in Figures 3.10a and 3.10b, respectively.

The second scenario investigates the system under the assumption of an immediate production stop from the year 2015 on. This leads to a peak of CNTs bound in the technosphere and a subsequent steady release (Figure 3.11 a,b).

The simulation results of the projected "growth"-scenario show a strong increase of both the amount of CNTs bound in polymer composites products and in landfill over time. The development of the material amounts in landfill is delayed relative to the material stock in polymer composites and shows a significant increase in the years from 2020 on. In the "production stop" scenario, the amount of CNTs bound in polymer composites slowly runs out, leaving only 5.09t in 2025. The total amount in landfill stabilizes at an amount of 7.63t at the end of the time considered, and the predicted soil concentration is 192 ng/kg. Both scenarios show relatively little uncertainty about the product stocks. In contrast, the spread between the 15% and 85% quantiles of the landfill stock is approximately the same as the mean value. Outliers even reach roughly three times the mean amount.

3.5. Discussion and Outlook

Dynamic probabilistic material flow modeling (DPMFA) as a new approach to material flow modeling provides a method for indirectly assessing material accumulations in stocks – both in the techno-sphere and in the environment – considering a variety of dependent partial flows and epistemic uncertainties. The simulation package to support the modeling process also provides components to represent local system behavior and a simulation environment to investigate dependent variables such as stocks at a particular time.

The suitability of the method and that of the Python package supporting it for modeling and simulating these systems were illustrated through their application to predicting stocks of engineered CNTs in the environment. This is an exemplary case and the new method is applicable virtually to all MFA and dynamic MFA modeling cases, e.g., the ones reviewed by Müller et al. (2014), if and when the modelers want to consider the uncertainties for all relevant model parameters.

The DPMFA method enables the assessment of environmental concentrations, exposure to humans and ecosystems, and emerging risks. Moreover, the implementation of the example model showed that in the case of CNTs, delayed material transfers and the existence of intermediate stocks in the technosphere have a large impact on estimated current and future environmental concentrations. Whereas it was possible before to perform such simulations with traditional dynamic material flow models, it was so far not possible to fully include the uncertainties of the model parameters. Considering the intermediate stocks enables a closer investigation of the actual material amounts released

to the environment and the prospective future releases. Within the scope of exposure assessment modeling, the new DPMFA method represents a significant step forward compared to established MFA methods because it allows consideration of a large range of different types of uncertainty for all relevant model parameters. The modeler can choose freely whether to use distributions, functions, or discrete data to describe the uncertainty of all parameters, thus making full use of the available data while representing the varying quantities and qualities of uncertainty as adequate as possible.

The time representation as a series of subsequent periods of equal length is an abstraction from the continuous nature of the flows in the real system. There are two good reasons for this abstraction. First, it enables efficient computation. Second, it corresponds to the way most data is available – as time series, namely as periodic (e.g., annual) values. Given that a continuous model would introduce assumptions (by implicit interpolation) that are often not warranted by data, this would induce a potential discretization error that would be rather inherent to the data than explicitly introduced during the modeling process.

The implementation of our approach as a Python package was chosen because it leads to several advantages. As a package on language level, it provides great flexibility for representing specific system characteristics, e.g., by implementing particular distribution functions for specific behaviors. The modeler is supported with virtually any parametric or non-parametric distribution function. As a tradeoff, programming skills are required. However, as Python is a language that is easy and convenient to learn, this disadvantage remains limited. At the same time it allows the modeler to embed the model into a larger project and to utilize the functionality of further associated libraries, e.g., for the preparation and management of large amounts of data with pandas (McKinney, 2014) or for plotting and evaluating simulation output with matplotlib (Hunter et al., 2007).

To ensure the computability also of larger models, the method accepts some limitations. The package does not support the representation of uncertainty about the time of a particular release from stock. However, material amounts in environmental stocks depend primarily on the total inflow to the system and the proportion transferred to the compartment. Especially for longer observation periods, the exact duration of a delay process has comparatively little impact on the total amount stored. Accordingly, uncertainty about these processes has only little influence and is therefore considered less relevant. Moreover, the transfer coefficients describing the relations between flows are considered stable over the investigated time (simulation length). Under this assumption, the model complexity mainly depends on the number of included model compartments and flow dependencies.

In general, the required computational effort to simulate a DPMFA model can be a limiting factor regarding model complexity, simulation length, time granularity, and desired precision of the simulation outcome. The used sample size of 50.000 illustrates a realistic, rather large sample, which leads to results that are stable between different simulation experiments. The computation of the model did not pose particular difficulties. Gottschalk et al. (2010a) the model stability of a PMFA model is discussed based on the match of significant numbers of the model output with the deterministic counterpart of the model as well as in between two simulation experiments of the same sample size. To estimate the required sample size for a particular precision of the results general estimations for Bayesian computation can be applied (Carlin and Louis, 2000).

For the given scope of the method – the assessment of environmental stocks and flows under substantial uncertainties – the simulation package was shown to be suitable. Considering a much higher degree of detail either of the system representation or the time resolution, might be desirable in some cases. However, a particular degree of detail of the model only makes sense if it is not considerably exceeded by the existing uncertainties.

As probabilistic – Bayesian – prediction models, our models represent incomplete knowledge about the true value of a parameter as probability distributions. To ensure to comprise the true parameter value, also wrong, but plausible values are included. Instead of a validation of the model in terms of confirming or rejecting it, it can be improved by proving or rejecting some of the assumptions made, which reduces the incorporated uncertainty.

Future work could provide additional components that are adapted to particular application domains. Moreover, the modeling process could be enhanced by higher-level modeling constructs, in particular for hierarchical modeling and graphic model representation. Also, while the actual processing of uncertain knowledge about material flows is clear, support for the modeler in the formulation of a probability distribution based on heterogeneous, diverse, and incomplete knowledge about a system variable could be improved.

Acknowledgement

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4

Representation, Propagation and Interpretation of uncertain Knowledge (Paper 3)

Original publication:

Representation, propagation and interpretation of uncertain knowledge in dynamic probabilistic material flow models

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Abstract

The determination of the environmental concentration of a pollutant is a crucial step in the risk assessment of anthropogenic substances. Dynamic probabilistic material flow analysis (DPMFA) is a method to predict flows of substances to the environment that can be converted into environmental concentrations. In cases where direct quantitative measurements of concentrations are impossible, environmental stocks are predicted by reproducing the flow processes creating these stocks in a mathematical model. Incomplete parameter knowledge is represented in the form of stochastic distributions and propagated through the model using Monte-Carlo simulation. This work discusses suitable means for the model design and the representation of system knowledge from several information sources of varying credibility as model parameter distributions, further evaluation of the simulation outcomes using sensitivity analyses, and the impacts of parameter uncertainty on the total uncertainty of the simulation output. Based on a model developed in a case study of carbon nanotubes in Switzerland, we describe the modeling process, the representation and interpretation of the simulation results and

demonstrate approaches to sensitivity and uncertainty analyses. Finally, the overall approach is summarized and provided in the form of a set of modelling and evaluation rules for DPMFA studies.

4.1. Introduction

Assessing environmental flows and concentrations of anthropogenic pollutants is a crucial step in determining emerging ecological risks of these pollutants. Because for many pollutants quantitative measurements are not feasible, material flow analysis (MFA) (Baccini and Brunner, 1991) and environmental fate modeling (MacLeod et al., 2010) have been developed to provide indirect means for exposure assessment. Based on the material inflow into a system, i.e. based on data on production of chemicals or materials, their use in particular products and subsequent pathways through the technosphere and the environment, environmental flows and stocks can be estimated and environmental concentrations over time derived.

However, for many pollutants, uncertainties about the underlying transfer and fate processes compromise model reliability and the suitability of the models to predict environmental stocks and concentrations. Scenario analysis has been used to investigate systems under different sets of uncertain assumptions (Huss, 1988; Bunn and Salo, 1993; Erdmann and Hilty, 2010). Nonetheless, scenario analysis does not include the assessment of the likelihood of a particular parameter setting.

Bayesian techniques provide methods to explicitly represent uncertain knowledge from various uncertain sources (Cullen and Frey, 1999). Diverging assumptions about the value of a model parameter are weighted based on the modeler's degree of belief and combined into a probabilistic parameter distribution. The results derived from Bayesian models are concluded based on the assumptions and their weighting. In Bayesian networks (Pearl, 1985; Ahmadi et al., 2015), which are the most widespread Bayesian models, parameters are represented by discrete sets of values and assigned probabilities.

In MFA, uncertainty handling can improve the credibility of a model and open it to a larger range of applications. However, most of the existing methods and tools provide uncertainty handling only based on simple error propagation or on a limited number of parameter distribution functions, e.g. in Umberto (ifu Hamburg GmbH, 2014) and STAN (TU Vienna, Institute for Water Quality, Resource and Waste Management, 2012). Probabilistic material flow analysis (PMFA) (Gottschalk et al., 2010a) has been developed to assess a system of pollutant flows as a steady-state system and to

represent and propagate parameter uncertainties using Bayesian modeling techniques. In PMFA, uncertain knowledge is represented using continuous probability distribution functions and the assumptions are propagated with Monte-Carlo simulation. In dynamic probabilistic material flow analysis (DPMFA) (Bornhöft et al., 2016), we extended the static approach of PMFA to consider sequences of consecutive periods and derive absolute stocks based on the periodic flows. DPMFA – as well as other Bayesian approaches – aims to include all plausible assumptions about a system dimension in a parameter distribution.

The main drawback of Bayesian approaches is, however, the increased modeling effort, i.e., to gather, weigh up and combine all plausible information about a model parameter. General approaches merging data from several sources under epistemic uncertainty have been discussed in the field of information fusion (Dubois and Prade, 2004; Smets, 2007). Bayesian belief functions (Smets, 2005) provide a representation formalism that seems suitable for parameter uncertainty.

The goal of Bayesian modeling approaches is to enable prediction modeling based on best knowledge. However, the specific impacts of the individual assumptions on a simulation result are not directly visible anymore. This is where sensitivity and uncertainty analyses (Loucks et al., 2005) are useful. They determine the relative impact of the model parameters, e.g. a transfer coefficient (TC) of a flow relation, on output variables, e.g., environmental stocks (Saltelli et al., 2008). There are several sensitivity analysis techniques in use (Hamby, 1994), of which "direct" differential sensitivities investigate the robustness of the model output variable with regard to a parameter variation. Uncertainty analysis methods such as the sensitivity index and the importance index (Hoffman, 1983) look at the impact of parameter uncertainty on the uncertainty about an output variable. The importance index ranks parameters based on their range to the total variance of the output value. Based on the specific impact of the model parameters, the most influential ones can be identified and further investigated.

While there is a wide range of methods to model incomplete knowledge and perform sensitivity and uncertainty analyses, there is no specific guideline for DPMFA yet. In (Gottschalk et al., 2010a) and (Gottschalk et al., 2010b) sensitivity analyses for probabilistic material flow models were performed ad hoc by decreasing the mean value of a of model parameter by 10% and calculating the resulting relative change of the observed model output variable. Uncertainty analysis was done by multiplying the standard deviation of a parameter distribution with the respective parameter sensitivity.

Exposure assessment of engineered nanomaterials (ENM) constitutes a good example do-main for modeling anthropogenic pollutants. Even though new detection methods

for ENM have been under development for some time, e.g., by Mitrano et al. 2012, a generic quantitative measurement of environmental concentrations is currently not feasible (von der Kammer et al., 2012). Instead, different modeling methods have been applied for the indirect assessment of different nanomaterials, such as MFA by Mueller et al. 2008 and Keller et al. 2013, and probabilistic MFA by (Gottschalk et al., 2010a; Gottschalk and Nowack, 2011; Sun et al., 2014; Gottschalk et al., 2015). In Sun et al. (2015) and 2017 we applied DPMFA to assess the environmental stocks of several ENMs in the European Union over time.

In this work, we will discuss the DPMFA modeling and evaluation process in detail and apply it on a case study for assessing environmental stocks of carbon nanotubes (CNT) in Switzerland as a proof of concept. Within that, a particular focus is set on the representation of uncertain system knowledge and the different types of model parameters and the robustness of particular modelling decisions. Moreover, the characteristics of a sensitivity analysis for DPMFA models are discussed, and the impacts on the predicted evolving stocks are analyzed. Finally, based on the impact of the uncertainty range of the particular model parameters and their value ranges, a set of scenarios is developed with the goal to explain the uncertainty of the model output as large as possible with only a small number of assumptions about model parameters.

4.2. Materials and Methdos

CNT Case study model

The significant flow processes of CNT through the technosphere into the environment are represented as a DPMFA model (Bornhöft et al., 2016). This model consists of flow compartments, stocks, sinks and external inflows. Based on the interplay of these compartments over time, the local material accumulations can be derived. The flows between the compartments are determined by local transfer coefficients (TCs) that define the flow from one compartment to another as a rate of its total outflow. This system of local flow dependencies distributes the inflows entering it. The time-dynamic behavior of the system is represented over a set of discrete, subsequent periods (i.e., years). For each period, system inflows are determined and the resulting internal flows and changes in stocks calculated. Moreover, delay functions define the residence time of the material in stocks and the subsequent release rates.

Incomplete knowledge about the actual values of system inflows and transfer coefficients is represented in the form of Bayesian probability distributions assigning non-zero

relative likelihoods to all plausible parameter values. The dependent model output variables are calculated based on these input distributions with Monte-Carlo simulation.

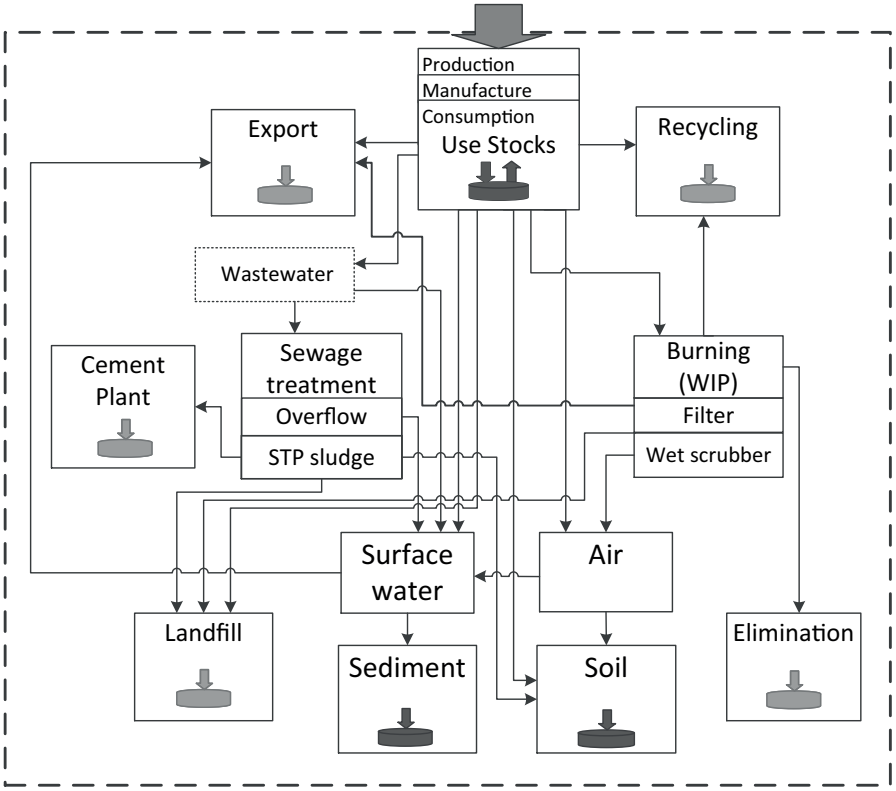


Figure 4.1: Schematic and simplified model structure. The production, manufacturing and consumption including the product use-stocks are combined into one box, as well as the sewage treatment and the waste incineration processes. The sinks in environmental compartments are represented in dark gray, the technical sinks in light gray. Arrows represent flows between the compartments. A complete description of all model compartments and transfers is provided in the supporting information

The model is implemented using the DPMFA simulation package described in (Bornhöft, 2015). The package provides a ready-to-use simulation infrastructure to perform Monte-Carlo simulation experiments and to evaluate a model for a given set of parameter distributions. It also provides a set of white box components for creating a model by implementing and assembling a specific system behavior. The parameter distributions can be defined either by selecting among mathematical distribution functions or by providing samples.

In the case study, the system investigated to illustrate the DPMFA modeling process

covers the material flows of CNTs from the year 2003 to 2020. The object of interest is the material accumulating in the stocks over time, in particular in the two environmental compartments sediment and soil. The evaluation of the stocks is demonstrated for the years 2012 and 2020 to cover both an assessment of past values and a prediction for the near future. An exemplary in-depth investigation is demonstrated for the predicted sediment stock in the year 2020 by performing uncertainty and sensitivity analyses.

The model structure (Figure 4.1) and the subdivision of the system into model compartments and the parametrization of the transfer coefficients are derived from a steady-state model by Sun et al. 2014 and have been used as starting point for the dynamic model described in Bornhöft et al. 2016. The model includes the production of the CNTs, the manufacturing of products containing CNTs, technical processes such as sewage and waste treatment and the receiving environmental media. This model was extended for the present study by in-use stocks for three of the modeled product categories – polymer composites, consumer electronics and automotive to represent the dynamic system behavior. Assumptions about production volumes of CNT are gathered for 2012 from various sources and scaled based on Piccinno et al. 2012, where historical production volumes are provided. In total, the model consists of 31 compartments, including the 3 use-stocks, 7 sinks, and 58 transfer coefficients.

Uncertainty representation and evaluation

Incomplete knowledge about the transfer coefficients and the annual production volumes is represented in the form of Bayesian parameter distributions. The choice of suitable distributions combining information from different sources of varying credibility and ways of representation is based on concepts of information fusion (Smets, 2007; Destercke et al., 2009). We will describe the transfer of these principles to DPMFA in the following paragraphs.

The robustness of the model regarding different modeling decisions and handling of incomplete knowledge is investigated for (i) the implicit uncertainty range that is added to values originating from data sources that do not explicitly provide information about uncertainty and for (ii) the explicit weighting of data from sources of different credibility. For both aspects, variants of the basic model are investigated. To assess the respective contribution of the model parameters to the output variables, direct differential sensitivity analysis is applied. As a deterministic method, it eliminates stochastic influences on the simulation outcome. This analysis is therefore not done with the given stochastic model, but with a deterministic counterpart created by using the parameter

distributions' mean values. (We will return to the stochastic model later.)

$$c_1 = \frac{\delta x_1}{\delta y} \tag{4.1}$$

Sensitivity coefficients (Eq. 4.1) indicate the correlation of a variation of a parameter x_1 and the corresponding change of a model output variable y. Based on the different parameter types of DPMFA, the applicability of differential sensitivity analysis is discussed and applied.

The absolute influence of the uncertainties in the model parameters on the output is calculated as the difference between the mean values of the investigated output variable y for the minimum and the maximum value of the parameter distribution x_1 (Eq. 4.2).

$$dependentRange(y) = abs(y_{x(min)} - y_{x(max)}) \tag{4.2}$$

The relative uncertainty range regards the dependent output range in relation to the mean of the output distribution as the most likely prediction. To identify the origin of the uncertainty of the variable y, the dependent uncertainty ranges for all parameter distributions $x_1 \ldots x_n$ are determined. By ranking the parameters according to their contribution to the variables' uncertainties, the most important ones are determined.

Based on the parameters that introduce the largest uncertainties, scenarios are developed. The scenarios aim to reduce most of the model uncertainties to a few assumptions and make their impact explicitly visible. Therefore, instead of using the investigated parameter distribution to simulate the model, we are using a high, a low and an average deterministic value, each out of the distribution. The .05 and the .95 quantiles are used as high and low values. In a subsequent step, the scenarios are combined to investigate the combination of assumptions.

4.3. Method Application and Results

This section demonstrates the modeling, simulation and evaluation process along an example application provided by the case study. It focusses on the choice of model parameters for the different system input variables, the interpretation of the model output, particular modeling decisions and their robustness. Moreover, sensitivity and uncertainty analyses are discussed. Along these steps, the procedure, observed results and their inherent implications are explained in detail.

4.3.1. Model design and simulation

The DPMFA modeling process aims to support the model builder in representing incomplete system knowledge regarding external material inflows, internal transfers and delay processes as model parameters explicitly. The model builder is intended to represent the uncertainty of parameters in a realistic and comprehensive way. Based on the uncertain parameters, the dependent model variables for the environmental sinks are calculated and the robustness of some general assumptions is investigated in the simulation process.

External Inflows External inflows to the model are defined as absolute volumes. Uncertainty is represented in the form of parameter distributions. In the CNT case study, we defined the annual material production as the source. However, data about actual production volumes is sparse. In particular for the years further ago, there are only isolated values for some of the periods. In contrast about the more recent past more data source are available. Therefore, from the sources about the recent periods, one comprehensive parameter distribution was developed for the year 2012 as the reference year. Based on a study stating the development of production volumes over time (Piccinno et al., 2012) (production volumes of CNTs for Europe and the world, extrapolated to Switzerland based on GDP), scaling factors were defined to adjust the distribution of the reference year to the other years. Scaling factors for missing and future volumes were obtained by extrapolation of the available data (SI 1.6). To generate the parameter distribution for 2012, in a first step, available data sources are gathered and the relevant assumptions worked out, then weighed against each other, and finally merged to a combined distribution. That way, a compromise had to be found between the one-by-one representations of the data sources and a model-wide consistent scheme. The following steps are performed to transform the available data into this form:

- Given likelihood distributions (e.g. observations or samples from previous simulation steps) are used unchanged.
- Ranges of plausible values are represented as uniform distributions.
- Single values are represented as triangular distributions, with the value given by the study as the mode value μ and a specific support. The support represents an implicit, plausible value range defining the min- and max-values of the triangular distribution. This value range includes additional assumptions about the given precision of the value and general considerations about the domain. In the CNT

case study we use a support of +- 0.5 of the mean value μ, reflecting the large uncertainties of the domain.

Based on the credibility of a data source (e.g., the reliability of the method that was applied in a scientific study or the review process published values have gone through), a relative degree of belief (DoB) is assigned to it. The combined probability distribution of the model parameter is created by merging the single distributions. Depending on the DoB of the data sources, samples of different size are merged into the combined non-parametric distribution to weight their respective impact.

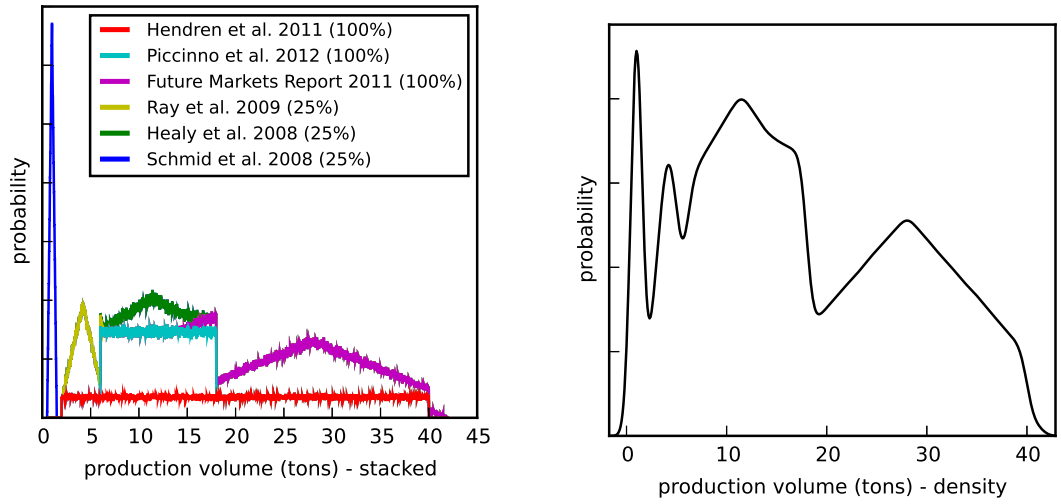


Figure 4.2: Combined belief function for the production volume of CNT in 2012. Diagram (a) shows histograms that were sampled from the likelihood distribution of each single study, weighted and added up. Diagram (b) shows a density function of the combined sample.

Figure 4.2 shows the combined parameter distribution of the production volume for 2012 for the case study. Each color displays the share from a particular single distribution, representing the respective weighted share of the data published in one reference. In Figure 4.2a, the single distributions are weighted and stacked. In this case, three of the distributions were assumed to have a degree of belief of four times of the other ones and weighted accordingly. The resulting overall distribution of the production volume is shown in Figure 4.2b. The combined sample is used as parameter distribution for the CNT flow model. The likelihood distributions of the dependent model variable are inferred from these parameter distributions using a Monte-Carlo simulation process. In

a subsequent step, the robustness of the model regarding more similar or more diverse DOBs as well as different supported ranges of plausible values are discussed along the modeling results.

Transfer Coefficients Parameter distributions for transfer coefficients (TCs) are developed in a way similar to that of the external inflows. However, here a different implicit support is assumed for data sources that only state a single value. As for the absolute system inflows, these values are modeled as triangular distributions with the value referred to in the data source as mode μ.

The implicit uncertainty range of a stated value of a TC is based on its minimum distance to 0 or 1. This means that very large and very small TCs are assumed to be less uncertain. For stated TC values ≤ 0.5 the min and max parameter of the triangular distribution are chosen around the stated values as mean μ and a parameter range from $\mu - 0.5\mu$ and $\mu + 0.5\mu$. For stated $TCs > 0.5$ a range of μ–$(1 - \mu)$ to $\mu + (1 - \mu)$ is chosen.

Analogous to the parameter ranges of the system inflow, the parameter ranges of the transfer coefficients include implicit assumptions about the precision of assumptions made within the domain. More specific knowledge about a transfer would lead to different ranges of implicit plausible values.

For the case study, we illustrate the CNT removal efficiency of sewage treatment plants (STP) which determines the proportion of the CNTs in the plant that is transferred to STP sludge, i.e., does not remain in the treated water. The parameter distribution is generated from four data sources displayed as diagram in the supplementary information (SI, Figure B.1).

Delay times The development of stocks over time is determined by the material inflows and residence times. The material residence times are parametrized as delay functions that define rates and the time lags after which particular amounts are released from a stock based on the time the material was accumulated. Unlike for other model parameters, deterministic release functions are used to represent delay times. In the case study, main delays are determined by the CNTs being bound during the lifetimes of the products they are used in before they are further released (SI Table B.2). As an example of these delay parameters, the residence time of CNTs bound in the "automotive" product category is estimated based on the lifetime distribution of automobiles. Based on a mean value of 11.9 years (Kraftfahrt Bundesamt, 2003) a normal distribution was used with a standard deviation of 5 years (Restrepo, 2015). Figure 4.3 shows the relative

annual release rates computed by a year-wise integration of the distribution function. The annual releases from the stocks contribute to the total model-wide mass flow of CNTs that is calculated for each period.

The discretization of the continuous material releases from stocks into periods of one year length is a simplification. However, it corresponds to the way most data is available, for example annual production volumes, and thus appears to be a suitable assumption.

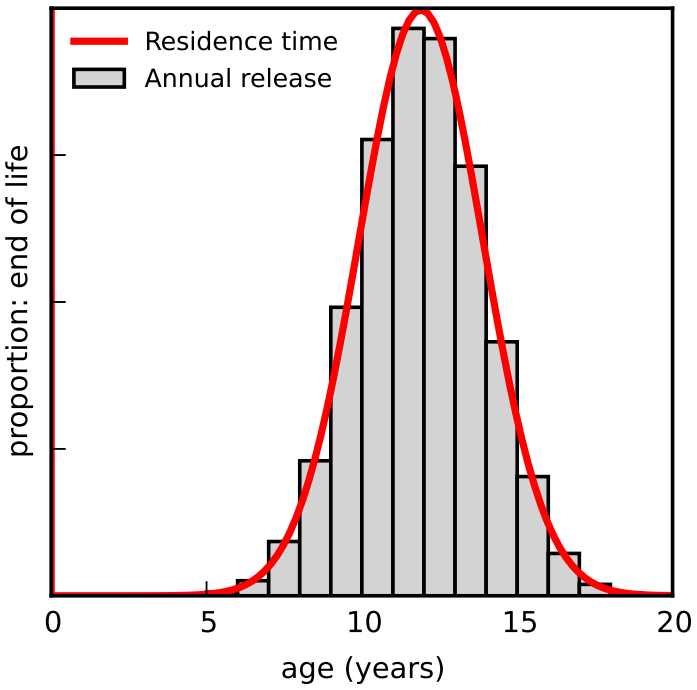


Figure 4.3: Relative residence time distribution of CNTs from the "Automotive"- use stock.

4.3.2. Model Output

The output of DPMFA models is calculated in a Monte-Carlo simulation process that propagates the inherent likelihoods of the parameter distributions to the dependent variables such as the material stocks at a particular time. These dependent values are made available as samples, whose distribution reflects the likelihood of particular values for the model variable. Figure 4.4 exemplarily illustrates a density function of the CNT amount accumulated in sediment for the year 2020. It reveals the shape of the function

as well as mean and mode values and the .15 and .85 quantiles.

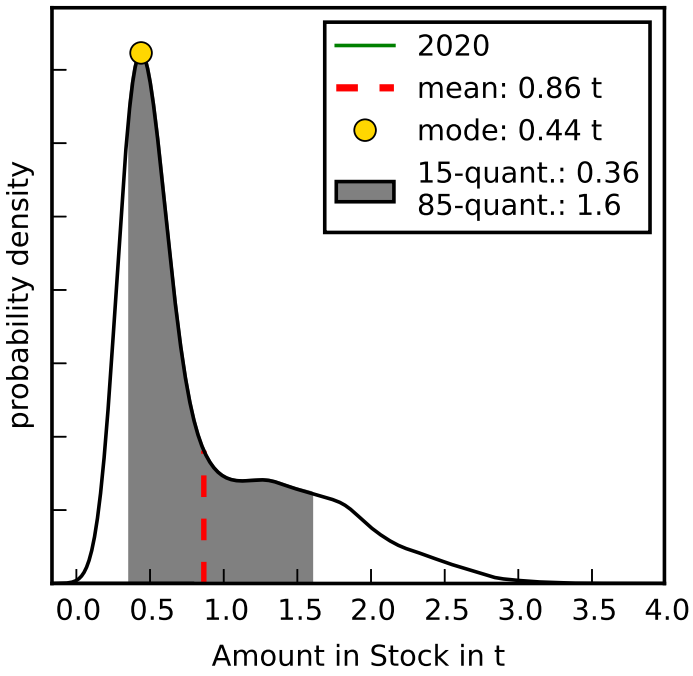


Figure 4.4: Projected density function of the CNT sediment stock in 2020

Table 4.1 summarizes the model stocks for the years 2012 and 2020 to provide estimations for a year with higher data availability and a forecast for a future period.

Uncertainty is indicated here by providing the .15 and the .85 quantiles in addition to the mean value. The comparison of the stocked amounts shows that a large part of the CNT is bound in product in-use stocks, 48.9 t in 2012 (182 t in 2020). The remaining shares describe amounts that already reached the final model sinks. The material amounts accumulated in environmental media are 0.35 t in soil in 2012 (2.15 t in 2020) and 0.18 t in sediment in 2012 (0.86 t in 2020). The proportion of the material eliminated by waste incineration by that time is much larger, 6.91 t in 2012 (70.3 t in 2020). Large amounts also end up in technical compartments, especially 12.7 t (63.75) in recycling. The further fate during recycling was not considered in this work but a first model is available describing the flows out of recycling for selected product categories and nanomaterials (Caballero-Guzman et al., 2015).

Table 4.1: Model stocks for the years 2012 and 2020 with mean values and .15 and .85 quantiles: In-use stocks (grey background), elimination (red), environmental media (green), and technical compartments (blue).

	2012			2020		
	.15-quant.	mean	.85-quant.	.15-quant.	mean	.85-quant.
Composites	28.09	41.09	54.57	107.79	151.54	195.74
Electronics	1.91	5.33	8.87	7.22	19.90	33.18
Automotive	0.86	2.50	4.25	3.77	10.63	17.92
Elimination	5.21	6.91	8.65	54.78	70.33	85.95
Soil	0.26	0.35	0.45	1.68	2.15	2.63
Sediment	0.07	0.18	0.33	0.37	0.87	1.62
Cement Plt.	0.02	0.06	0.10	0.12	0.29	0.43
Recycling	6.96	12.68	18.60	38.48	63.75	89.94
Export	1.47	3.12	4.83	8.71	16.17	23.88
Sum	44.85	72.22	100.65	222.91	335.62	451.25

4.3.3. Robustness of modeling decisions

As models are representations of a system, idealized for a specific purpose, good modeling decisions focus on the aspects that are decisive for the system behavior under study while abstracting from others to reduce model complexity. The robustness of the simulation results with regard to the modeling and data handling decisions can be used to estimate if a modeling decision taken has considerable impact on the observed model outcome. This robustness reveals aspects of the model for which a more detailed representation of the investigated system could improve the model most to make it more realistic.

In the following, the robustness of the case study model is investigated regarding the data handling decisions made. In the original model, two types of data sources with different credibility stating values for the annual production volume are considered. The type that is considered more credible is weighted four times as strong as the other type.

Table 4.2 shows the impact of modeling alternatives on the predicted sediment stock in 2020. A stronger weighting of the differences, using a DoB of 1/10 for the data sources with less credibility leads to a mean predicted value of 0.94 t, 8 % more than with the basic assumption. An equal treatment of all sources, ignoring their different credibility results in a mean predicted stock of 0.64, 26.4 % less than the original model.

For the second modeling decision, we take a closer look at is the assumption of the implicit support for values which are based on a single data source. Table 4.3 compares the parameter setting of the original model with an increased and a reduced uncertainty range, each by 50 % of the original range. Changes of the original assumption of an

Table 4.2: Alternative modeling of the annual CNT production volumes: mean value and .15 and .85 quantiles for the predicted CNT-Stock in sediment in 2020 weighting the less credible data sources with a 10 % DoB of the more credible ones (row 1) and an equal DoB of all data sources (row 3).

	.15 Quant.	mean	.85 Quant
DoB of more credible data sources 10x the lower ones	0.4	0.94	1.72
Original model	0.37	0.87	1.62
Same DoB for all data sources	0.26	0.64	1.17

Table 4.3: Alternative implicit uncertainty ranges for TCs: Predicted CNT-stock in sediment in 2020 providing the mean value and the .15 and .85 quantile

	.15 Quant.	mean	.85 Quant
Smaller implicit uncertainty range: $\mu + -0.25\mu$	0.37	0.86	1.59
Original model	0.37	0.87	1.62
Larger implicit uncertainty range: $\mu + -0.25\mu$	0.36	0.88	1.60

uncertainty range by increasing or reducing it by 50 % of the original range only lead to small changes of the resulting sediment stock in 2020 of 0.01 t (<2 %). This indicates a high model robustness regarding changes of the implicit support for parameter distributions of the TCs.

4.3.4. Sensititvity Analysis

Sensitivity analyses investigate the impact of a model parameter on an examined output variable. They allow identifying critical spots of the underlying system that can be addressed in actions to improve the system behavior. For the case study system, these are the processes that affect the development of the environmental CNT stocks. If the predicted environmental concentrations constitute a risk, these spots might be addressed to reduce the environmental exposure (Coll et al., 2016). DPMFA models include model parameters and variables of different dimensions. To allow a comparability, relative parameter changes based on differential sensitivity analyzes are investigated. Moreover, the specific characteristics of the different parameter types need to be considered to determine how and to what extent they are suitable for sensitivity analyzes.

Inflows, transfers and delays

System inflows are modeled for each year as stochastic likelihood distributions from a continuous value domain. They represent an absolute material inflow for each year. The independent parametrization of external system inflows for each period allows considering either a variation of the material inflow of a single period, or of all periods. As the main objects of interest in the example study are the accumulated stocks, we also focus on an even variation over all periods for the model input. However, for a closer examination, also other combinations, e.g. a variation of only future periods, could be investigated.

The sensitivity of the model stocks to a variation of the transfer coefficients shows the contribution of that transfer to the development of a stock. This can serve as an indication to find processes within the technosphere, where improvements could reduce the development of environmental stocks. A special characteristic of the method is the assumption of balanced mass flows. If one TC is changed, the TCs of the other flows coming out of the same compartments are normalized to maintain a mass-consistent system behavior. As the consequence of the increase of one flow, the remaining flows are decreased by the same amount. Negative correlations between TCs and stocks are determined by the consideration of mass conservation in the model (e.g. through normalization or direct dependencies). As the sum of all outgoing TCs from a compartment needs to be one, the assumption of an altered TC also implies the adjustment of other, dependent ones. However, to obtain the impact of TCs with several corresponding flows, it is more useful to regard the direct, positive correlations.

While parameters defining material amounts and transfer coefficients take values from a continuous domain (and may be varied by a particular rate), the time representation in DPFMA is discrete, which implies that delay parameters can only be varied in whole time periods. Therefore, a real differential sensitivity analysis to assess the influence of delay times is not possible. However, the overall impact of delay in a temporary stock can be estimated by increasing the delay time by one period and by calculating the model without any delay. An increased delay time of CNT bound in the Composite materials in-use stock of the case study would lead to a reduction in the 2020 sediment stock by 0.68 %. Assuming an immediate release from Composites leads to an increase of the sediment stock by 7.53 %.

Table 4.4: Sensitivity coefficients: correlation between relative changes of the model parameters and the material amount in sediment stock in the years 2012 and 2020. The displayed values mark the highest positive and negative correlations.

	Sediment 2012	Sediment 2020
Annual Production volume (System inflow)	1.01	1.00
TC: STP treatment ->Surface Water	0.65	0.64
TC: System inflow ->Production	0.53	0.52
TC: Production ->Waste Water	0.46	0.45
TC: System inflow ->Manufacturing	0.25	0.24
...		
TC: Air ->Soil	-1.83	-2.37
TC: Composites ->WIP	-1.17	-2.85
TC: System inflow ->Consumption	-77.4	-75.7

Sensitivity analyzes of the Case Study model

For the case study, a direct differential sensitivity analysis is performed varying all model parameters individually and observing all model stocks as listed in Table 4. The results are discussed in more detail for the sediment stock in 2020. To allow a comparison of the impacts of the parameter changes, they are displayed as relative values. Table 4 provides the largest positive and negative sensitivity coefficients for the case study model regarding the investigated sediments stocks in 2012 and 2020. A table of all correlations between the model parameters and output variables for environmental stocks for 2012 and 2020 is found in the supporting information (SI Table B.4).

The strongest positive correlation is found for the annual production volumes with 1.00 for 2020 (1.01 for 2012). This reflects the fact that the model only includes one external source from which all CNTs later accumulated in stocks originate from. It is followed by the sensitivity coefficient of the TC of the flow rate from the STPs compartment to the surface water compartment 0.64 (0.65) and the one for the rate being lost in the production process of 0.52 (0.53). Here, parameter changes have the largest influence on the Sediment stock as model output variable. Hence, improving the parameter TC STP treatment $-$ > Surface Water is most likely to improve the overall system most.

4.3.5. Uncertainty analysis

Uncertainty analysis is applied to determine the origin of the uncertainty about a model variable. For the case study, we investigated the impacts of the particular parameter distributions on the total uncertainty about the predicted sediment stock in 2020 in detail. For each model parameter, the model was simulated using the smallest and the largest value of the parameter distribution as a deterministic parameter value. The remaining parameters were kept unchanged. Figure 4.5 shows the resulting ranges of the predicted mean values. The precise values are listed in the SI (SI Table B.5).

The largest influence comes from the annual production, where the smallest volumes that are considered plausible lead to a most likely stock of 0.03 t and the highest one of 2.07 t, representing a range of 2.04 t. Referring to the predicted mean stock from the basic model of 0.85 t, this range is 240 % of the most likely assumption. The sewage treatment plant (STP) efficiency introduces an uncertainty range of 1.63 t (191 %) followed by the TC of the allocation from material consumption to paints 0.47 t (55 %), consumption to polymer composites 0.32 t (37 %), and manufacturing to waste water 0.18 t (21 %).

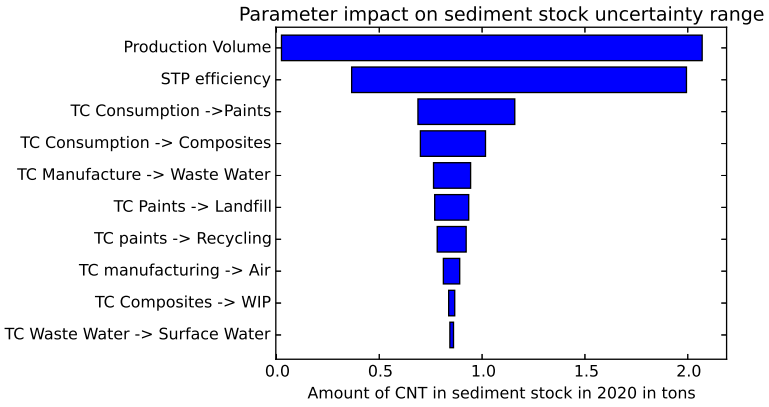


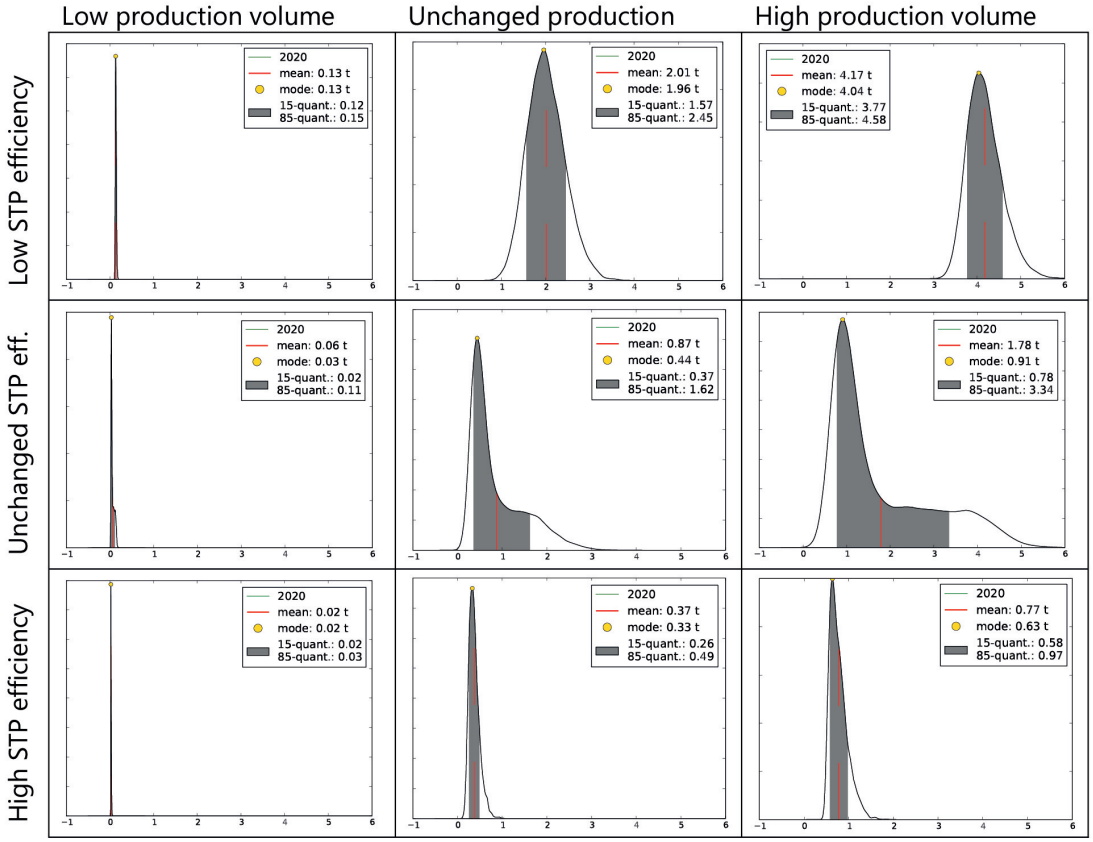
Figure 4.5: Impact of the model parameter ranges on the predicted environmental stock of CNTs in sediment. The bars describe the range from the expected mean in sediment from the minimum to the maximum value of the range of the parameter distributions.

After uncertainty analysis on a basis of single parameters, the impact of combinations of particular assumptions can be investigated. Therefore, for the model parameters with the largest uncertainty contribution to the investigated model variable, both a low and a high assumption are considered. For the CNT flow model the uncertainty about the predicted emerging sediment stock in 2020 is strongly determined by the uncertainty about the true material production volume and the STP efficiency. Hence,

these parameters are investigated more in detail.

From both parameter distributions, the .5 and the .95 percentile are taken as plausible low and high assumptions. These assumptions and combinations of them are investigated as different scenarios (Figure 4.6). The high production scenario leads to double the amount of CNT in the sediment stock for 2020 of the basic model, 1.78 t and also a much broader uncertainty range. A low STP efficiency would most likely lead to sediment stock of 2.01 t while the combination of a high production and a low STP efficiency results in a mean prediction of 4.17 t – 479 % of the basic prediction. A low production volume leads to a strongly reduced predicted stock of 6.9 % (2.3 % in the high STP and 19.9 % in the low STP efficiency scenario).

Figure 4.6: Scenarios investigating high and low production volumes and STP efficiencies; for the low STP efficiency scenario the .05 percentile and for the high STP efficiency scenario the .95 percentile from the respective distribution are used. The production scenarios use the .05 and the .95 percentile from the production distributions of every year. The other parameter distributions are left unchanged. For each scenario the probability density function of the sediment stock in 2020, its mean, and mode, as well as the .15 and .85 percentiles, are given.



4.4. Discussion

The proposed procedure for model design, sensitivity and uncertainty analysis specifies a series of concrete modeling and evaluation steps for predictive modeling of environmental concentrations of anthropogenic pollutants using DPMFA. This way it makes the modeling process transparent and helps to assess the obtained results. Moreover, the CNT case study provides a comprehensible hands-on illustration as an example for a long-lasting anthropogenic pollutant. Table 4.5 summarizes the main modelling and evaluation steps.

The DPMFA approach uses Bayesian knowledge representation to reproduce epistemic system uncertainties. It allows predicting environmental stocks including the inherent uncertainties. However, as a drawback, it raises the overall modeling effort and the need to explain the obtained results compared to deterministic approaches. Standardized steps from information fusion formalize and streamline the shaping of parameter distributions and help to cope with the rising complexity. Nevertheless, they also allow introducing more complex parameter distributions where existing system knowledge requires it.

Sensitivity analyses identify the main drivers of a dependent system variable. They can serve as a preselection of entry points for measures to reduce environmental stocks and concentrations. Besides a general reduction of the material production, the improvement of sewage treatment and the reduction of losses during production processes have been identified to affect the resulting stocks of the case study model most. However, as the model includes uncertain assumptions, the applied deterministic differential sensitivity analysis focusing on the means of the distributions is subject to these uncertainties. In particular, this needs to be taken into account in cases where the examined parameters include wide value ranges.

While deterministic flow models are validated within a particular precision and may later be falsified, rejected and replaced, DPMFA models (like all Bayesian models) are designed to include all plausible values to ensure, they cover the true value as well (Nowack et al., 2015). Improved system knowledge reduces parameter uncertainty - if a system dimension is known with a higher level of certainty, the parameter distribution representing it becomes narrower and also the information derived from the model more definite. The impact of these parameter uncertainties on the model output values was determined using uncertainty analysis. For the case study, the production volume of the material and the STP efficiency introduce the largest uncertainty about the predicted sediment stock. An increase of knowledge about these parameters proposes the largest

Table 4.5: Objectives and implementation of the modeling and evaluation steps in DPMFA studies

	Aim / research subject	**Application in DPMFA**
Model Development and Simulation	Prediction of stocks of the investigated substance and the environmental exposure	Identification of decisive stock and flow processes, Representation of all available system knowledge as parameter distributions Application of a clear and transparent standardized modeling process, Robustness checks for important design decisions to determine their impact on the model outcome
Sensitivity analysis	Drivers of the emerging environmental concentrations Entry points for improvements measures	Calculation of sensitivity coefficients between the model parameters and the investigated output variable, Parameter mean values as basis
Uncertainty analysis	Contribution of the parameter uncertainty to the overall uncertainty of an output variable Identification of points, where better data can improve the model most.	Calculation of output ranges of an investigated model variable for each individual parameter between a high and a low quantile of the parameter distribution, Consideration of scenarios combining the assumptions from the parameters with the highestuncertainty contribution

reduction of uncertainty about the sediment stock. Combining high/low scenarios for these two parameters provide quite clear predictions under the given assumptions.

4.5. Conclusion

Applying a rule-based, structured modeling process and sensitivity and uncertainty analysis can increase the conclusiveness of a DPMFA study and provide a more complete picture about the investigated system and the derived model. The derived results provide predictions about environmental stocks and related risks, while the sensitivity analyses identify points for measures to reduce the environmental impacts and uncertainty analyses show where further findings could contribute the most to a reduction of uncertainties. This way, dynamic probabilistic maternal flow analysis can become an even more meaningful tool for environmental risk assessment and a valuable approach to estimate hazard to ecosystems through anthropogenic pollutants.

Acknowledgement

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5

Application to Model the Emissions of Different ENM for the EU (Paper 4)

Original publication:

Dynamic Probabilistic Modelling of Environmental Emissions of Engineered Nanomaterials

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Abstract

The need for an environmental risk assessment for engineered nanomaterials (ENMs) necessitates the knowledge about their environmental concentrations. Despite significant advances in analytical methods, it is still not possible to measure the concentrations of ENMs currently in natural systems. Material flow and environmental fate models have been used to fill this gap and to provide predicted environmental concentrations. However, all current models are static and consider neither the rapid development of ENM production nor inclusion of the fact that a lot of ENMs are entering an in-use stock and are released from products (i.e. have a lag phase). Here we use a dynamic probabilistic material flow modelling to predict former, current and future flows of four ENMs (nano-TiO_2, nano-ZnO, nano-Ag and CNT) to the environment and to quantify their amounts in (temporary) sinks such as the in-use stock and ("final") environmental sinks such as soils and sediments. Given the rapid increase in production, this approach is necessary in order to capture the dynamic nature of ENM flows. The accumulated masses in sinks and the average concentrations in technical compartments quantified in our study provide necessary data for risk assessors and scientists in need of quantitative knowledge on the presence of ENMs in various compartments. The flows to the environment that we

provide will constitute the most accurate and reliable input of masses for environmental fate models which are using process-based descriptions of the fate and behaviour of ENMs in natural system but rely on accurate mass input parameters.

5.1. Introduction

Previous modelling efforts have attempted to show the concentration of ENM in environmental and technical compartments (Blaser et al., 2008; Boxall et al., 2007; Mueller and Nowack, 2008; Gottschalk et al., 2009; Johnson et al., 2011; Keller et al., 2013; Gottschalk et al., 2013b; Sun et al., 2014; Keller and Lazareva, 2013).However, all the models published so far are static and do not consider time-dependent processes with respect to the use and release of ENMs. The current models consider only the input by production, manufacturing and consumption (PMC) into the system that occurs in one year and subsequently distributes the mass over the entire system in the same year. The models also assume that all ENMs produced are released to waste streams and environmental compartments in the same year that they enter the system and so in this way no in-use stocks are considered. With these two oversimplifications of the true situation, the static models do not represent the actual ENM flows to environmental compartments under conditions where a rapid increase in production of ENMs is taking place and when they are entering in-use stocks. Moreover, the static models cannot predict concentrations in environmental sinks, such as soils or sediments, because these compartments accumulate inputs over many years. First attempts in considering accumulation in environmental sinks have been made by Gottschalk et al. (2009) who used a very simplistic model to scale the input in previous years to calculate final concentrations in soils and sediments. Sun et al. (2015) made a spatio-temporal prediction of mass-flows and concentrations for five ENM in biosolids amended soils in South Australia over a period between 2005 and 2012. However, both of them only considered one aspect of the dynamic nature of the system a periodic production inputs into the system, but another aspect the delayed ENMs release from in-use stock is completely missing. A realistic prediction of ENM flows to the environment therefore requires a complete dynamic material-flow analysis model (MFA). Unlike the static models, a dynamic MFA is able to track the flows over many years and it also no longer uses the simplified assumption of immediate ENM release. Dynamic MFA is a well-established modelling technique. Müller et al. (2014) performed a review on dynamic MFA methods with respect to uncertainty treatment. More than half of the methods covered did not consider uncertainty at all; 37% used

sensitivity analysis, Gaussian error propagation (6%) or parameter ranges (5%), but none supported a full probabilistic uncertainty representation. The dynamic probabilistic MFA (DP-MFA) method recently developed by Bornhöft et al. (2016) is able to fill this gap. This method represents all system dimensions under uncertainty as probability distributions in the respective model parameters and propagates these values to the dependent model variables using Monte-Carlo simulation. The aim of this work was to build a customised DP-MFA model based on this new method for four ENM - nano-TiO_2, nano-ZnO, nano-Ag, and CNT - and predict their former, current and future mass-flows to technical and environmental compartments and the resulting concentrations in these compartments.

5.2. Methods

5.2.1. General principle

The general principle of the DP-MFA model for the four ENMs can be summarised by the following three features: 1) dynamic considerations, 2) the use of a life-cycle concept and 3) a probabilistic approach. The dynamic feature distinguishes the current model from all previous static models by a more realistic representation of the true system dynamics as developed by Bornhöft et al. (2016). The dynamic considerations in this study are comprised of two aspects: the input dynamics and the release dynamics. The input dynamics describe the annual production of ENMs as inflows into the system within a given period. The release dynamics describe the time-dependent ENM release kinetics from a specific product category over the entire life-cycle.

Following a life-cycle concept, the model tracks the ENM mass-flows from ENMs production to incorporation into the commercial product and finally from the products to technical and environmental compartments during/after their use and disposal (Mitrano et al., 2015). Probabilistic methods are employed for all the parameters used in the modelling processes to address the inherent uncertainty in the raw data used (Gottschalk et al., 2010a). This means data from varied sources, with inherently different reliability, are combined into an appropriate probability density distribution. The input data for the model are the annual production amounts of ENMs in the EU, the estimated shares of ENM applied onto product categories, the process-based transfer coefficients within and among the technical systems and the transfer coefficients between environmental compartments. All these parameters are treated as appropriate probability distributions depending on the data available. For each of the parameters, 100,000 random iterations

are made to represent the comprehensive picture of the probability density distribution as described in the previous study (Gottschalk et al., 2010a).

The scheme of the DP-MFA is shown in Figure 5.1. It consists of two modules: the "Release Module" and the "Distribution Module". The Release Module addresses the input and release dynamics. It describes the annual ENM production/consumption entering the system, the estimated share onto product categories, the flows from product categories by immediate release or into in-use stocks and finally the release from in-use stocks. The total annual release of ENMs is then transferred to the compartments of the "Distribution Module". The Distribution Module is built upon the previous static model (Sun et al., 2014), which describes the ENM transfers within and between technical and environmental compartments.

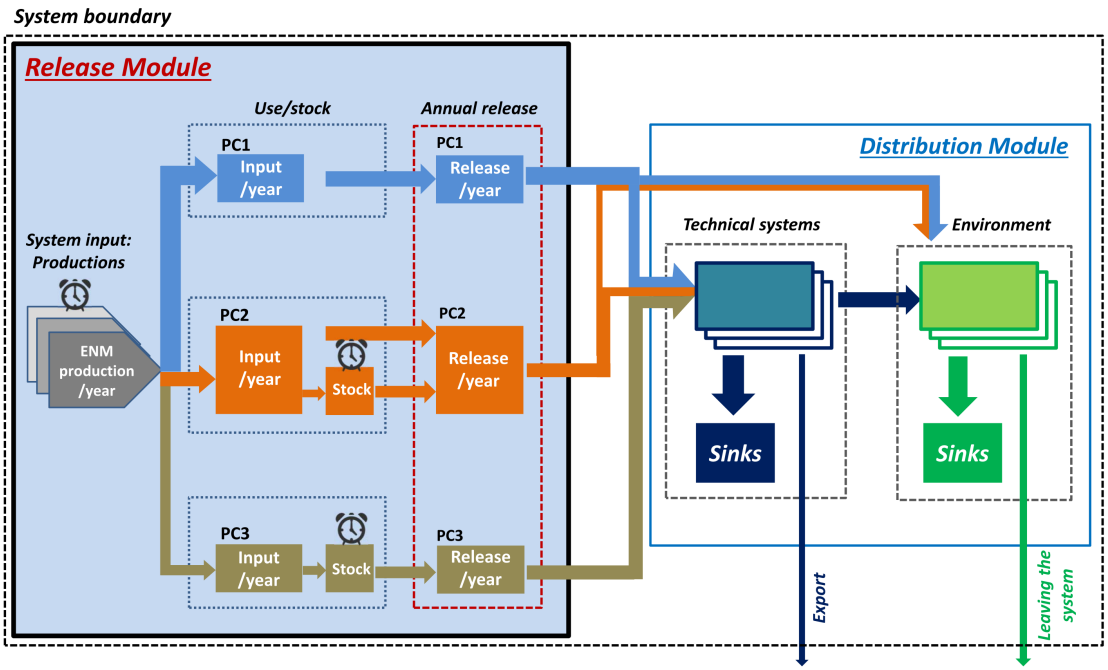
System boundary

The geographical focus of this study is the European Union (EU) due to the abundant information available. But modelling for other regions can be easily expanded once data needed are provided. The technical compartments included in this study are landfills, sewage treatment plants (STP), waste incineration plant (WIP), recycling and export. The environmental compartments considered are atmosphere, natural and urban soils, sewage sludge treated soils, surface waters and sediments. Among these compartments, landfills, soils and sediments are defined as sink compartments. From sink compartments no downstream flows are modelled. A study by Caballero-Guzman et al. (2015) was included providing an explicit description of ENM fate during and after recycling processes.

In this study we track the mass of the initial ENMs. Transformed ENMs (in our definition which lose their nano features i.e. gasification, dissolution, chemical reactions) will be viewed as loss of the ENMs and flow to a virtual compartment called "Elimination".

Input dynamics

We considered a time frame from 1990 to 2020. Explanations of the definition of the time frame are given in the Supplementary Information (SI). The estimation of production of ENMs over time is made by multiplying the base year production (2012) with retrospective and prospective scaling factors. The production of the four ENM in 2012 is based on the probability distributions provided by Sun et al. (2014) updated with newly available data. Table S1 shows the raw data used for building the probability distribution of the ENM production in 2012. The scaling factors for each individual year are based



PC: Product Category; **Technical systems:** landfills, sewage treatment plants, waste incineration, recycling, export

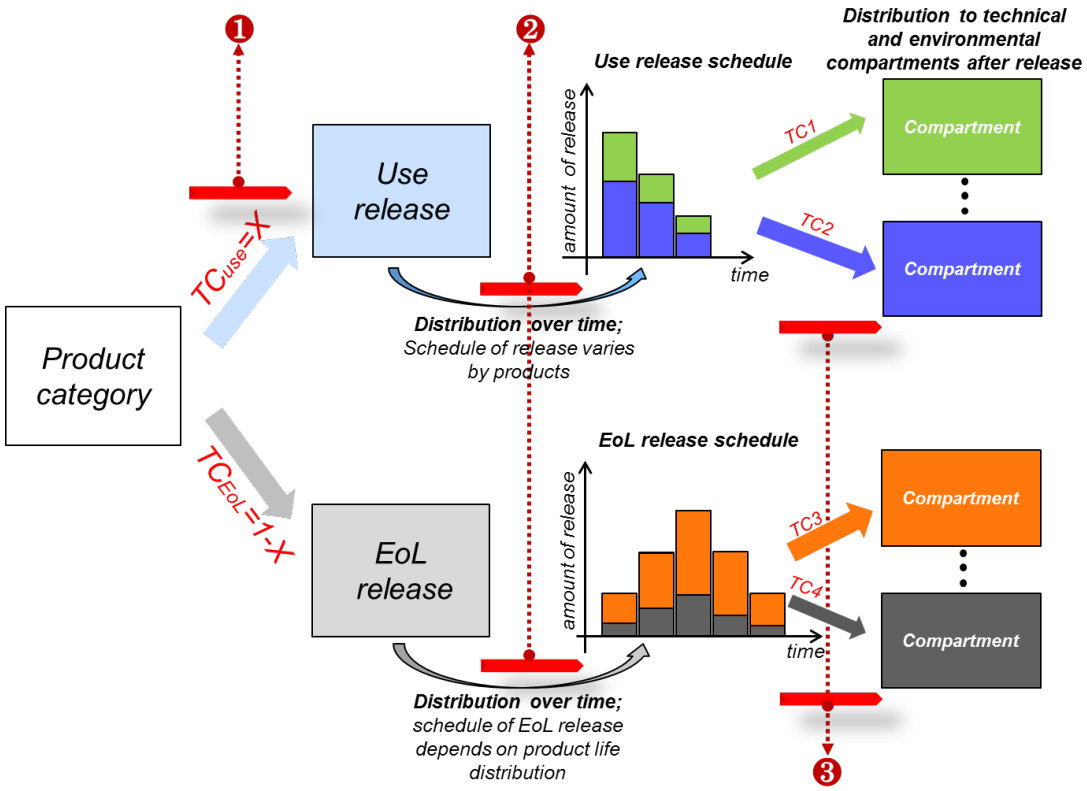
Figure 5.1: Schematic of the probabilistic dynamic material flow model for ENMs. It consists of two modules, the Release Module and the Distribution Module. The Release Module focuses on dynamic system behaviour, describing both the input dynamics and the release dynamics. The Distribution Module describes ENM distributions within and between technical and environmental systems after they are released out of the use phase.

on ENM market projections, nanotechnology patent analysis, and direct information on ENM production (Piccinno et al., 2012) when available. We use the assumption that the development of ENM production is proportional to nanotechnology development with respects to e.g. patents registrations, funding etc. A summary of all the data used for estimating probability distributions of the scaling factors are summarised in Table S2. The probability distribution of ENM production in 2012 and the distribution of scaling factors are multiplied to obtain the probability distribution of ENM production for the period from 1990 to 2020.

For nano-Ag, an additional estimation of the production development for a period from 1900 to 2020 has been made. This longer time period is founded in the historic applications of "silver colloids" that are in fact nano-Ag. (Nowack et al., 2011) Detailed information on how this is done can be found in the SI.

Release dynamics

"Release" in our definition refers to ENM that leave the production, manufacturing, and consumption phase and are transferred to technical or environmental compartments. The total ENM production is assigned to different nano-enabled product categories in shares based on the information provided by a previous study. (Sun et al., 2014) This allocation of ENM to product categories is assumed to remain constant over the time considered in this study. Figure 5.2 shows the scheme of how time dependent ENM release from products is expressed in the model. It proceeds in three steps: separation of ENM allocated to one product category into the "Use release" and "End of Life (EoL) release" ❶, scheduling of Use and EoL release ❷, distribution of ENM to technical and/or environmental compartment after Use release and EoL release ❸.



TC: Transfer Coefficient; **EoL:** End of Life

Figure 5.2: Schematic visualization of the time dependent ENM release dynamics. For ENM contained in a product category, the first step ❶ is the division of the total ENM-content between the "Use re-lease" and "EoL release". The ENM contained in a product category allocated to "Use release" is the fraction supposed to be released during its use phase; the part allocated to "EoL release" is the fraction supposed to be remaining in the product and be released once the products come to their end of life. The second step ❷ is the definition of the duration of the "Use release" and the "EoL release" as well as the release schedule; in other words in how many years the release events take place for one product category and how much of the fraction is released each year. The "EoL release" depends on the life-time distributions of each product category; here normal distributions are assumed. The third step ❸ is the distribution of the released ENM from the scheduled "Use release" and "EoL release" to technical and environmental compartments.

5.3. Results and discussion

5.3.1. ENM production over time

Figure 3a shows the modelled production development of nano-TiO_2 in the EU between 1990 and 2020. The corresponding diagrams for nano-ZnO, CNT and nano-Ag are given in Figure S2. The full probability spectrum of the production development is used as main input for the dynamic flow modelling. The grey lines represent single model runs with single values randomly selected out of the underlying probability distributions. The denser the grey lines appear, the more likely the modelled value is true. The mean values are shown by the red line. The uncertainty can be quantified by the width of the gap between the 15% and 85% quantiles (dashed blue lines).

5.3.2. Release dynamics

Table 5.1 depicts the dynamic release parameters for nano-Ag as an example. Data for nano-Ag was shown here as an example because relatively more extensive information is available. The respective data for the other ENMs are given in the SI. This table demonstrates the division of the release between Use release and EoL release, the release schedule over time and the allocation to different compartments after release. As Table 5.1 shows, important products categories such as Electronics and appliances, Medtech and Paints have the major part of nano-Ag remaining in the product and it is released when it reaches the end of life. In contrast, product categories like Textiles, Cosmetics, Foods, Cleaning agents and Plastics have their nano-Ag component released mainly during the use phase.

Product life times are often independent of the ENM application, therefore they are either well known or can be easily estimated. The release kinetics of ENM is specific to which ENM is applied to and how the material is bound to a product. This information is based preferably on experimental data when it is available or estimated on the basis of expert judgement. The use of realistic data compared to worst-case assumptions (Boxall et al., 2007; Mueller and Nowack, 2008; Gottschalk et al., 2009; Johnson et al., 2011; Keller et al., 2013; Sun et al., 2014; Keller and Lazareva, 2013) ensures a realistic modelling effort.

Product categories of Electronics and Electricals, Plastics, Paints, Metals and Filters have life-times normally longer than 5 years. With 20 years of use release, Metals is the product category with the longest use release. Electronics and appliances, the most important product category for nano-Ag, has an average life-time of 8 years. (Streicher-

Porte, 2014) Fast release is found in non-durable product categories for instance Cosmetics, Foods, Cleaning agents and Medtech. For these, we have estimated general use release duration of 1 to 2 years. Experimental studies indicated that the majority of nano-Ag release takes place in the early stage of their life-time.(Limpiteeprakan, 2014; Kaegi et al., 2010) Therefore, in the use release schedule release is mostly allocated to the first year. Most nano-Ag released during use release end up in waste water, which was evaluated on the basis of a previous study (Sun et al., 2014).

In our approach, the EoL release schedule of ENM for a product category is represented by its life-time distribution, i.e. the time it takes until it is discarded. The longest EoL release is estimated for Paints. Although, Paints have an average use release duration of 8 years, the EoL release duration is in average 80 years, governed by the life-time of the buildings they are applied to. (Hischier et al., 2015; ATD Home inspection, 2014) Complete use release in the first year is assumed for product categories with fast use release, such as Foods, Cleaning agents and Medtech. Distribution of nano-Ag to landfill, WIP, recycling and export after EoL releases are made according to solids waste management statistics in the EU for general solid waste (Bakas et al., 2011) and specific waste (Kiddee et al., 2013; EEA, 2012; Friend of the Earth Europe, 2013; EEA Website, 2013; Glass International, 2014; ERPC, 2011).

		❶	❷						❸				❶	❷	❸			
Priority (share of the total nano-Ag application)[a]	**nano-Ag** (product categories)	*Use release*	*Use release duration (years)*	*Use release schedule*					*Distribution after use release*[b]				*EoL release*	*Lifetime distribution (normal) Note: σ is the standard deviation*	*Distribution after EoL release*			
		X		*Y1*	*Y2*	*Y3*	*Y4*	*...*	*Waste water*	*Air*	*Surface water*	*Soil*	*1-X*		*Landfill*	*WIP*	*Recycling*	*Export*
38.1%	Electronics & Appliances	0.30[b]	8[c]	1/8[d]					1.00				0.70[b]	mean=8; 3σ=8[c][d]	0.09[e]	0.06[e]	0.65[f]	0.2[g]
25.1%	Textiles	0.60[h]	3[i]	0.7[h]	0.2[h]	0.1[h]			0.80	0.20			0.40[h]	mean=3; 3σ=2[i]	0.31[i]	0.07[j]	0.28[i]	0.34[j]
10.2%	Cosmetics	0.95[b]	2[d]	0.9[d]	0.1[d]				0.90		0.10		0.05[b]	Y1=0.90, Y2=0.10[d]	0.35[e]	0.25[e]	0.40[k]	
6.6%	Foods	0.90[a]	1[d]	1.0[d]					1.00				0.10[a]	Y1=1.0[d]	0.6[e]	0.4[e]		
6.0%	Cleaning agents	0.95[b]	1[d]	1.0[d]					1.00				0.05[b]	Y1=1.0[d]	0.35[e]	0.25[e]	0.40[k]	
3.6%	Medtech	0.05[d]	1[d]	1.0[d]					1.00				0.95[d]	Y1=1.0[d]		1[d]		
3.3%	Plastics	0.80[d]	8[d]	1/8[d]					1.00				0.20[d]	mean=8; 3σ=5[d]	0.35[e]	0.25[e]	0.40[k]	
3.0%	Paints	0.35[l]	7[m]	0.9[l]	0.1*(1/6)[d][l]				0.50	0.25		0.25	0.65[l]	mean=80; 3σ=20[n]	0.3[d]		0.7[o]	
2.4%	Metals	0.05[b]	20[d]	1/20[d]					1.00				0.95[b]	mean=20; 3σ=5[d]	0.03[e]	0.02[e]	0.95[l]	
0.6%	Glass & Ceramics	0.35[l]	10[d]	0.9[l]	0.1*(1/9)[d][l]				1.00				0.65[l]	mean=10; 3σ=5[d]	0.20[e]	0.10[e]	0.7[p]	
0.6%	Soil remediation	0.98[d]	1[d]	1.0[d]								1.00	0.02[d]	Y1=1.0[d]	0.6[e]	0.4[e]		
0.3%	Filter	0.30[a]	8[m]	1/8[d]					0.80	0.20			0.70[a]	mean=8; 3σ=8[m]	0.09[e]	0.06[e]	0.65[f]	0.2[g]
0.2%	Diapers	0.05[d]	1[d]	1.0[d]					1.00				0.95[d]	Y1=1.0[d]		1[d]		
0.1%	Paper	0[d]											1.00[d]	mean=5; 3σ=4[d]	0.07[e]	0.03[e]	0.7[q]	0.2[q]

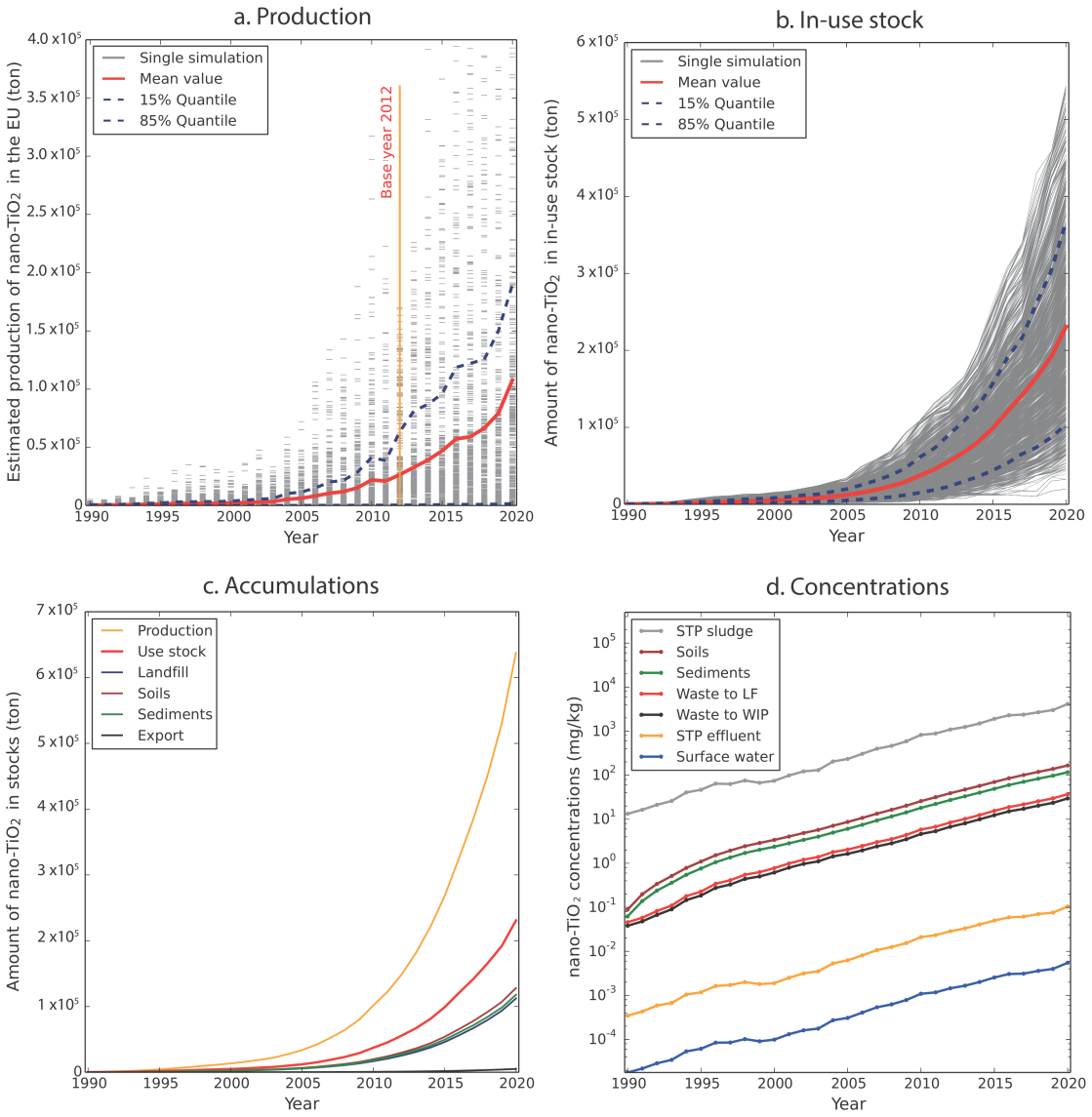
(a) Sun et al. (2014), (b) Revised based on Sun et al. (2014), (c) Streicher-Porte (2014), (d) Expert judgement, (e) Bakas et al. (2011), (f) Kiddee et al. (2013), (g) EEA (2012),
(h) Limpiteeprakan (2014), (i) EEA Website (2013), (j) Friend of the Earth Europe (2013), (k) EEA (2009), (l) Kaegi et al. (2010), (m) ATD Home inspection (2014), (n) Hischier et al. (2015), (o) EEA (2009), (p) Glass International (2014), (q) ERPC (2011)

Note: Yn = year n, e.g. Y1= year 1

Table 5.1: Summary of parameters for the release dynamics used in the model for nano-Ag; the respective information for nano-TiO2, nano-ZnO and CNT is provided in Table S3. The column Priority is based on the share of nano-Ag applied in the different product categories. Columns ❶, ❷ and ❸ correspond to the three allocation steps shown in Figure 5.2. Values of X in the column Use release in step ❶ indicate the fraction of nano-Ag contained in a product released during the use phase; values of 1-X in the column EoL release indicate the fraction of nano-Ag released at the product's end of life (EoL). Use release duration in step ❷ means the estimated number of years during which release takes place; Use release schedule in step ❷ describes during the use phase how much nano-Ag is released from a product each year; Distribution after use release and Distribution after EoL release in step ❸ contains information about the transfer coefficients defining the nano-Ag allocation to different compartments after release; the life-times of the products categories are assumed to be normally distributed. Average life-time and standard deviations are either based on literature if available or estimated based on expert judgement; 6σ is used to show the whole span of the life-time.

5.3.3. Evolution of ENMs in stocks and sinks

One of the reasons to conduct a dynamic modelling endeavour is to calculate the accumulated ENM loads in compartments that accumulate ENM. Figure 5.3b shows a full picture of the distribution of the nano-TiO_2 amount development in in-use stocks of product in the EU from 1990 to 2020. This is visualized by single simulation (grey lines) out of 100,000 runs with mean value (red line) and 15% and 85% quantiles (dashed blue lines). Figure 5.3c highlights the mean values for the accumulated production and the amount accumulated in the use stock, landfills, sludge treated soils and sediments. All the stocks exhibit an exponential-like increase over time. This is caused by both the accumulation in the compartment and the yearly increasing input into these stocks. Results for nano-TiO_2 were demonstrated here as an example because it is the most interesting ENM in terms of production size among the four ENMs.



LF=Landfill, **WIP**=waste incineration plant.

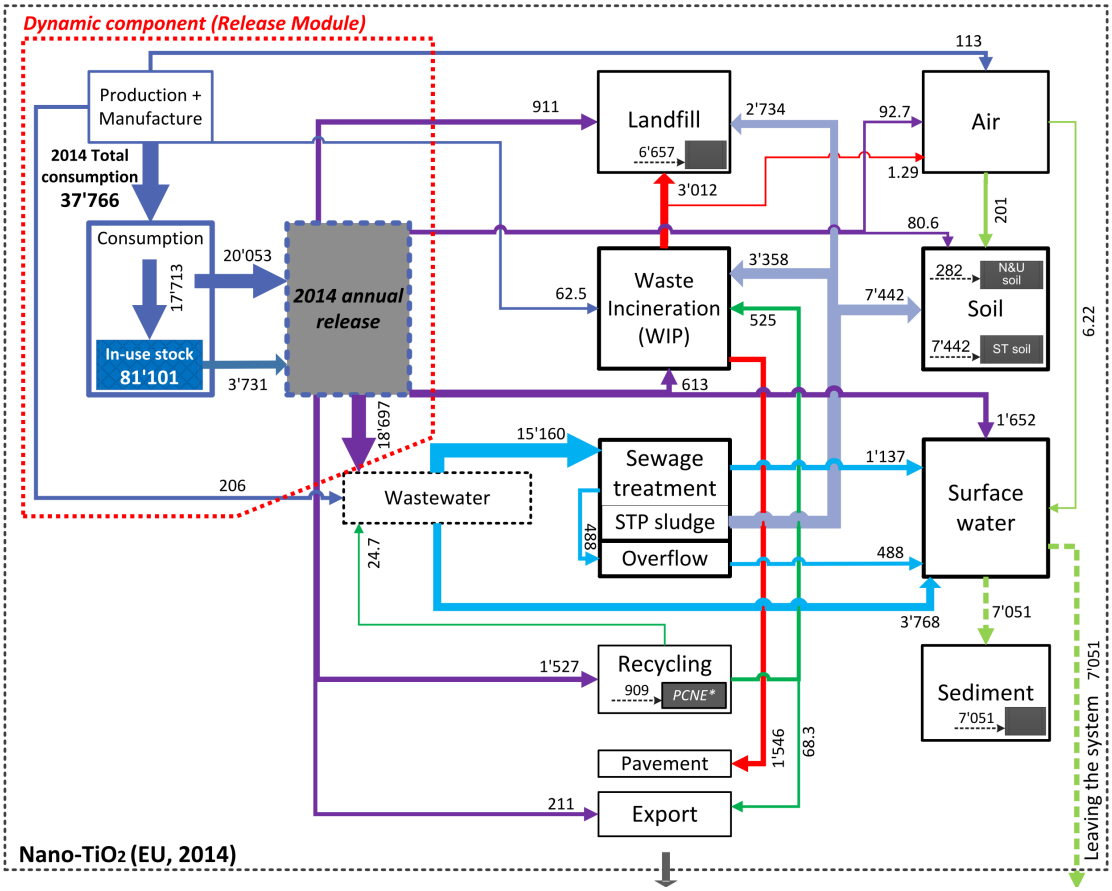
Figure 5.3: **a.** Modelled production development of nano-TiO_2 in the EU from 1990 to 2020. Short grey lines indicate the single modelled values. The red curve is the average trend of all simulated values. Dashed blue lines indicate the 15% and 85% quantile range of the probability density distribution of the production. **b.** The evolution of nano-TiO_2 amount in the in-use stock. The grey lines are development trend of a single iteration out of 100,000 simulation runs; here only 2,000 are shown. The mean (red trace) and 15% and 85% quantile are shown (blue traces). The whole cluster area consisting of grey curves builds up the range of the probability distribution of the overall trend. The vertical width of the grey area indicates the degree of uncertainty. **c.** Mean values of the evolution of nano-TiO_2 in the in-use stock and in landfills, sludge treated soils and sediments as well as the total accumulative production in the EU from 1990 to 2020. **d.** The evolution of the concentrations in selected technical and environmental compartments in logarithmic scale. "Soils" here indicate the STP sludge treated soils.

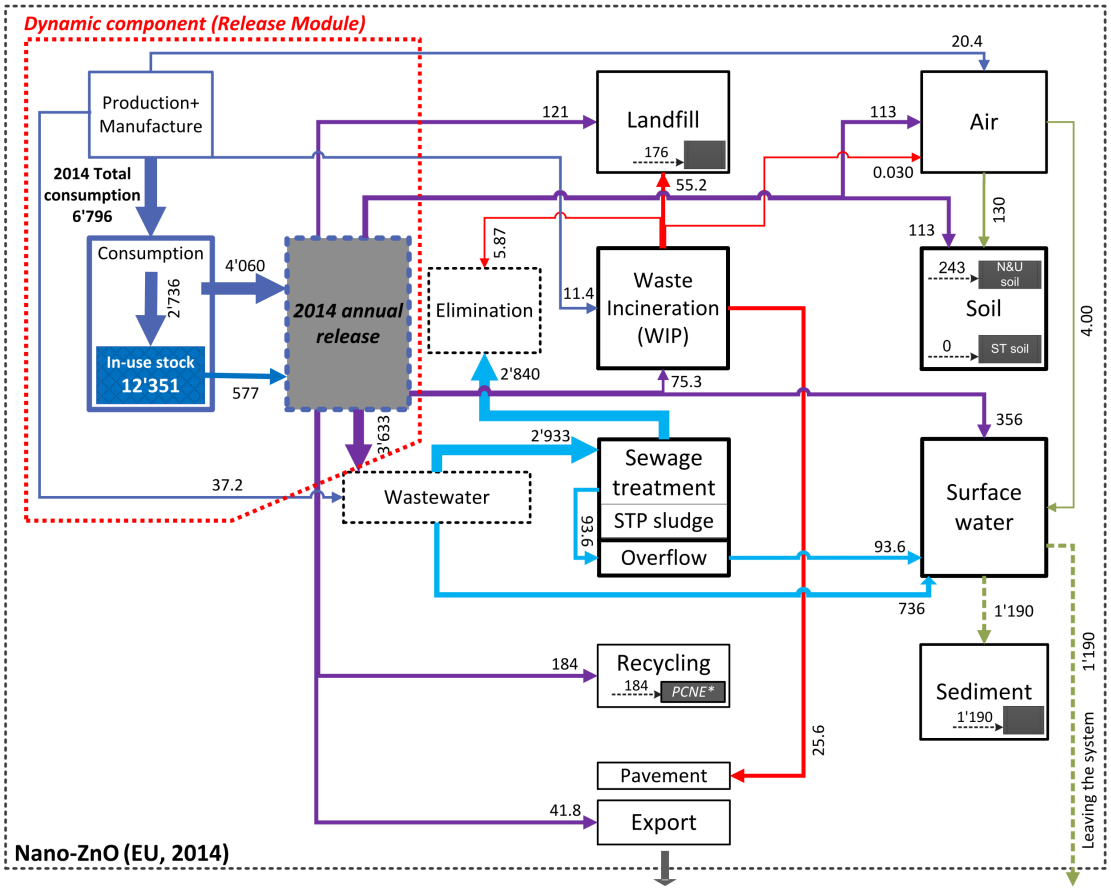
5.3.4. Mass-flows of ENM

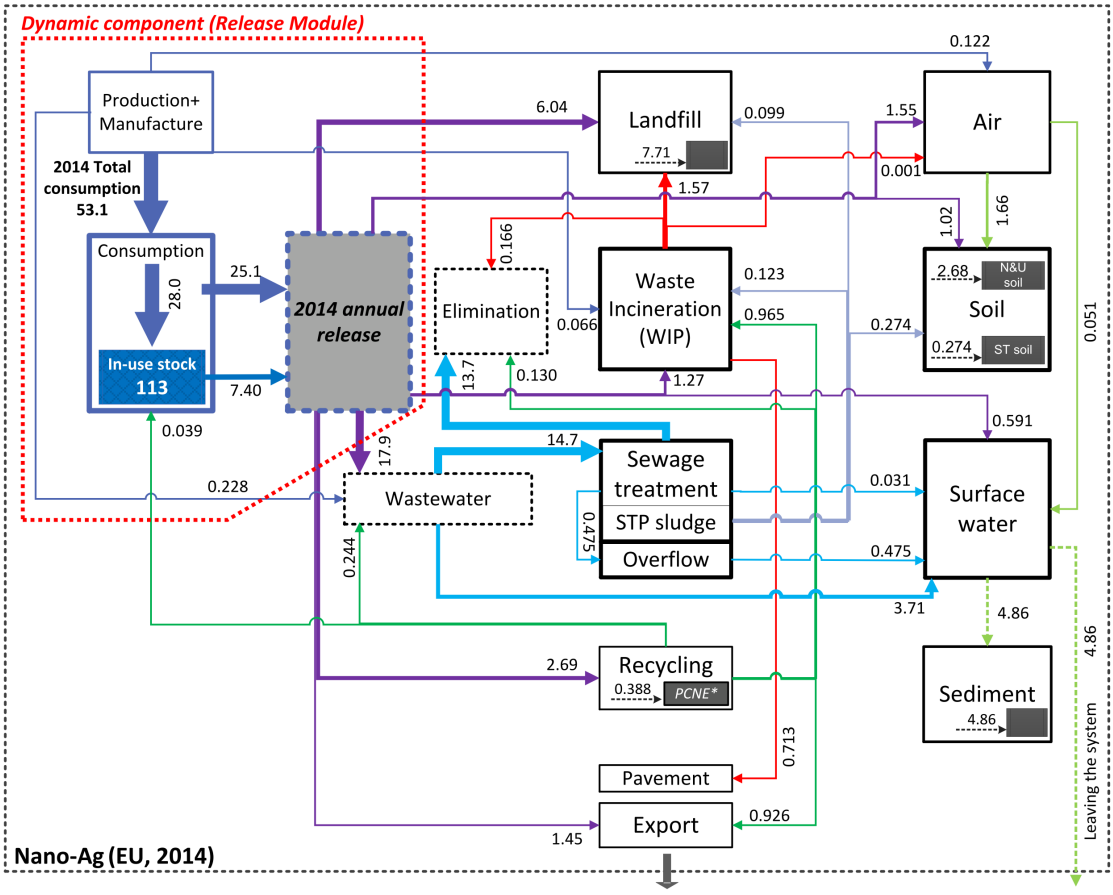
Flows of the four ENMs, from production and use through to release into all compartments, were modelled by combining the modelled production volumes, shares of ENM applied in products and transfer factors between all the compartments for the year 2014, incorporating the dynamics of the system from 1990 to 2014, as shown in Figure 5.4. The mean total productions of nano-TiO_2, nano-ZnO, nano-Ag and CNT estimated for EU in 2014 were 38'000, 6'800, 50 and 730 tonnes respectively. Depending on the products applying these materials, different shares of amounts currently produced are entering into in-use stock or are released into technical and environmental compartments. For nano-TiO_2, nano-ZnO and nano-Ag, about half of the year's total input into the system enters the in-use stock and the rest is directly released during the same year. With respect to CNTs, less than 1% (0.4 out of 730 tons) is directly released and nearly 100% is allocated to the stock phase. The amount in the in-use stock up to 2014 for nano-TiO_2, nano-ZnO and nano-Ag is in general around two times of their input in 2014; for CNT it is four times because the majority is stocked. Releases from in-use stock together with the immediate release from 2014's input constitute the total release in 2014. Compared to the immediate release, the release from stocks (previous year's input into the system) is in most cases much smaller, being about 15-25% of the total annual release. The one exception are CNTs, for which more than 99% of the annual release in 2014 is coming from in-use stock, again showing their particular applications in polymer nano-composites which corresponds with little immediate release. This importance of releases from in-use stocks justifies the need for a dynamic modelling of ENM. Because flows into a certain product category are split into stocked and released amounts, it is not possible to compare the new results to those of static models such as from Sun et al. (2014) or Keller et al. (2013) and Keller and Lazareva (2013). In these models the production in one year was completely distributed to the environment, an assumption that our dynamic modelling has clearly shown to be not representative for the ENM investigated.

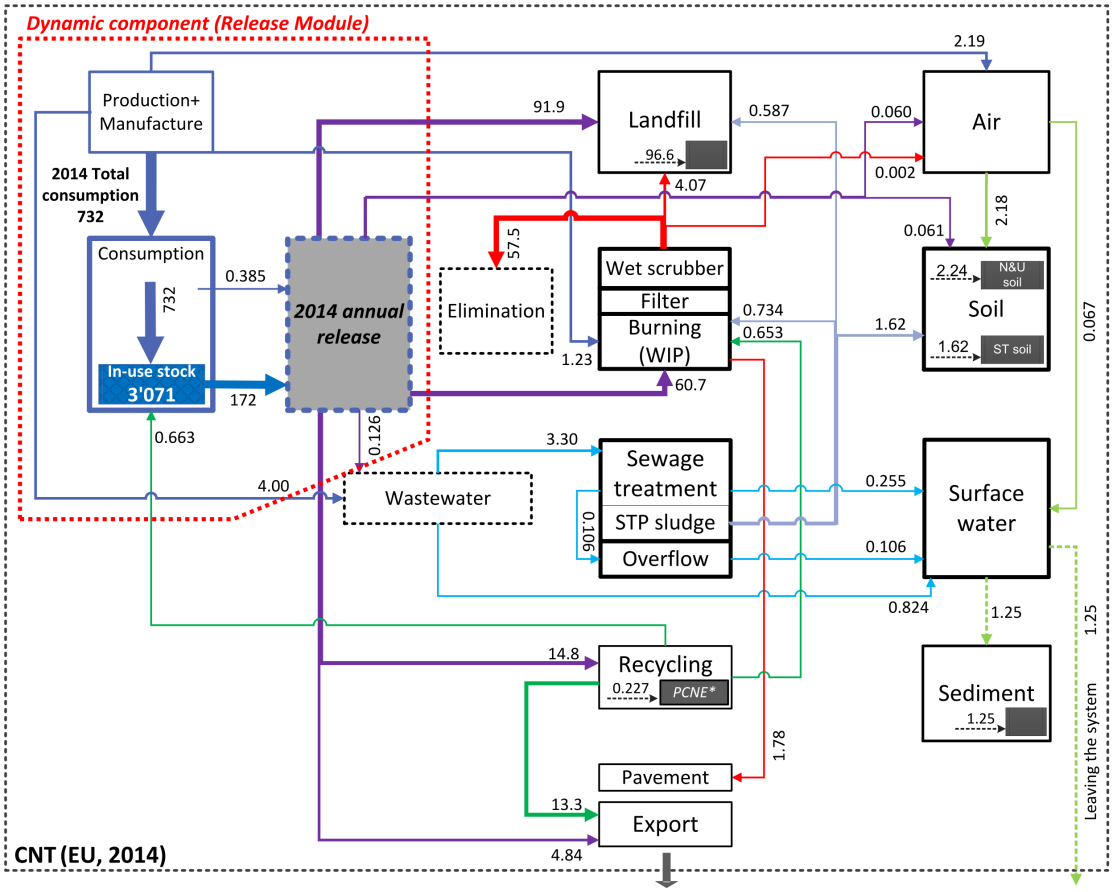
The most prominent flows for nano-TiO_2 and nano-ZnO after release were from production, manufacturing, and consumption (PMC) to wastewater (and further to STP). This is due to the fact that the major applications for these two ENM are in cosmetics (the priority columns in Table 5.1 and Table S3 shows the shares for all ENM applications). For nano-Ag, the major flows are from PMC to landfill and to waste water. The most prominent flows for CNT were from PMC to landfill, followed by the flow to WIP, and from there to elimination. This can be explained by the fact that most of these

materials are applied in polymer composites. ENM flows through the STP are mainly captured in STP sludge, and further transported to WIP and landfill, and some ENM end up in soil from sludge application. After wastewater treatment processes, nano-ZnO is transformed into different chemical forms such as ZnS, Zn sorbed to iron oxides and $Zn_3(PO_4)$ (Ma et al., 2013; Lombi et al., 2012) and thus allocated to the virtual elimination compartment. As mentioned above, after passing through wastewater transfer and treatment, most of the metallic nano-Ag is transformed to Ag sulphides and is therefore also ending up in the elimination compartment (and therefore left the system because the metallic nano-Ag property was lost.




Dynamic component (Release Module)
20.4
Production+ Manufacture
121
Landfill
176
113
Air
2014 Total consumption 6'796
55.2
0.030
130
113
Consumption
4'060
2'736
In-use stock 12'351
577
2014 annual release
5.87
Elimination
11.4
Waste Incineration (WIP)
243
N&U soil
Soil
0
ST soil
4.00
2'840
75.3
356
2'933
3'633
Sewage treatment
STP sludge
Overflow
37.2
Wastewater
93.6
Surface water
93.6
736
1'190
184
Recycling
184
PCNE*
Sediment
1'190
1'190
25.6
Pavement
41.8
Export
Leaving the system
Nano-ZnO (EU, 2014)


Dynamic component (Release Module)
Production+ Manufacture
2014 Total consumption 53.1
Consumption
28.0
In-use stock 113
25.1
7.40
2014 annual release
0.039
0.228
17.9
Elimination
0.166
0.066
13.7
0.130
Wastewater
0.244
6.04
Landfill
7.71
0.099
1.57
Waste Incineration (WIP)
1.27
0.123
0.965
14.7
Sewage treatment
STP sludge
Overflow
0.475
0.031
0.475
3.71
2.69
Recycling
0.388
PCNE*
Pavement
0.713
Export
0.926
1.45
0.122
1.55
Air
0.001
1.02
1.66
2.68
N&U soil
Soil
0.274
0.274
ST soil
0.591
Surface water
4.86
Sediment
4.86
0.051
4.86
Leaving the system
Nano-Ag (EU, 2014)



PCNE: "Product Categories Not Evaluated" by Caballero-Guzman et al. (2015), based on which the recycling process are modelled

Figure 5.4: Mass-flow of dynamic modelling of nano-TiO_2, nano-ZnO, nano-Ag and CNT in the EU for the year 2014 in ton/year. The nano-Ag flow chart displays the "1990-2020" scenario. The values for flow quantities are mean values from the respective probability distributions. The thickness of the arrows reflects the quantities of flows; the black squares in some compartments represent stocks in these compartments, e.g. in-use stock, landfill, soils, and sediments. Colours of flow arrows are only for differentiating flows. The dynamic component, the "Release Module", is highlighted with the red dashed line. The dashed lines from "Surface water" to "Sediments" or "Export" indicate worst case scenarios: either the ENM are completely transferred to sediments or are fully stable in water and are carried by water out of the system boundary (exported).

5.3.5. Concentrations

The compartments for which concentrations of ENM are calculated are assumed to be well-mixed and homogenous, although natural and urban soils and sewage sludge treated soils are differentiated. These concentrations are therefore representative for an average hypothetical region as defined in the REACH guidance (ECHA, 2012). All details about the parameters used are given in the Table S4. Table 5.2 shows the predicted ENM concentrations in STP effluent, surface water, STP sludge, air, solid waste entering landfill, solid waste entering WIP, WIP bottom ash and WIP fly ash, as well as accumulated concentrations in sediments, soils, and STP sludge treated soils for the EU in 2014. The values presented are the mean values, mode values, median values and the 15% and 85% quantiles (Q0.15 and Q0.85) from each distribution. This feature of our results is unique compared to other deterministic models because it allows assessing the range and the likelihood of expected concentrations. In general, for all ENMs, the highest concentration is found in STP sludge, followed by solid waste, WIP bottom ash and WIP fly ash. Among the environmental compartments (soil, surface water, air and sediments), sediments had the most considerable concentrations, followed by STP-sludge treated soil, then untreated soil and surface water, followed by air, with the lowest concentration of ENM overall. For soils and sediments, the simulations provided the accumulative amount of ENM deposited in these compartments in since 1990. In all the compartments considered, nano-TiO_2 had far higher concentrations than the other three ENMs. This reflects the correlation between the total input production volume and the consequent concentration in different compartments. Sediments, where most ENM entering surface water end up in our worst-case scenario, showed accumulated concentration ranging from 6.7 μg/kg (CNT) to nearly 40,000 μg/kg (nano-TiO_2). In most cases the concentrations in WIP materials (solid waste to WIP, WIP bottom ash and WIP fly ash) are at the "mg/kg" level.

Comparing the results for the concentrations of nano-Ag based on the two scenarios with different time scope, the results of the scenario with the time frame "1900-2020" are only slightly higher than the results of the scenario "1990-2020". For most compartments the difference is less than a factor of two. Larger differences are found in the accumulated amounts in sludge treated soils and sediments. There, the results from the scenario "1900-2020" are a factor of five larger than that of the scenario of depicting "1990–2020". Here, certainly the longer accumulation effect plays a role, although historic nano-Ag uses were modelled to be much lower than current ones.

With respect to recycling, unlike previous static modelling studies, we were able to

include the fate of ENM during recycling based a recent modelling study of ENM flows during recycling (Caballero-Guzman et al., 2015). Although in reality there may well be ENM in landfill leachates, our model did not take this account due to the insufficient quantitative information that exists on this process. It also needs to be noted that the concentrations in surface water and sediments reflect worst-case scenarios for both compartments. No fate modelling was performed and the water concentrations assume no sedimentation or other losses while the sediment concentrations reflect complete sedimentation from water. However, our flow results can be used as input data for dedicated mechanistic fate models that all rely on accurate predictions of the input flows.

Due to the different dynamic and static modelling concepts applied, it is not really possible to draw a direct comparison between the newly predicted concentrations results with all previous studies (Mueller and Nowack, 2008; Gottschalk et al., 2009; Keller et al., 2013; Sun et al., 2014; Keller and Lazareva, 2013; Sun et al., 2015). As stated in the mass flow section above, the previous models distributed the produced mass in one year to the whole system in that year while our dynamic modelling clearly revealed that in-use stocks and delayed releases are highly important and essentially define the system behaviour. However, this does not necessarily lead to lower predicted concentrations because releases from previous years are also considered and in some cases may dominate the flows. Similar concentrations in 2014 predicted by static and dynamic models may therefore by chance have the same magnitude. Extending the simulation time will reveal larger and larger differences between the two approaches due to additional releases from stocks.

The values presented in Table 5.2 include both the uncertainty in some of the parameters as well as the variability that is caused by the representation of a range of different forms of an ENM (e.g. coatings, functionalization), which are subsumed under the label of a generic ENM, e.g. nano-TiO_2. In our approach, single numbers are treated with a deviation factor of two and with triangular distributions. Data for which a range is given are treated with uniform distributions. Normal and other distributions are used alone or combined in accordance to available data. This treatment of the available data allows us to consider for each parameter the knowledge that is available by including always the specific uncertainty associated with each parameter. The major purpose of the dynamic modelling is to track the historical concentrations and project the future concentrations of ENMs in accumulative compartments. Therefore, besides the ENM concentrations predicted for the year 2014, we also provide the concentrations in 2020 in Table S5. Additionally, predicted evolutions of ENM concentrations in major compartments are provided in Figure 5.3d and Figure S2d. These predictions are based on the combined

estimates of different market research companies and are grounded in the increase in the market in the last years and are probably valid if the technology continues to develop as it does today.

5.3.6. Considerations for the applicability of model results

The concentrations that we provide for the technical compartment, e.g. wastewater, sludge or bottom ashes, can be used as input values for more sophisticated environmental fate models that incorporate a mechanistic description of fate processes, e.g. agglomeration and sedimentation. Praetorius et al. (2012) for example used the ENM mass flow to natural waters from Gottschalk et al. (2009) as input to their mechanistic river fate modelling of nano-TiO_2. Also, Gottschalk et al. (2011) used the release from wastewater as input for a local modelling study with high spatial resolution of ENM within the Swiss river network. In another example using the same dataset, Dumont et al. (2015) used for their spatial modelling on ENM in European watersheds. Meesters et al. (2014) took the emissions data to air, water and soils from the Mueller and Nowack (2008) mass-flow model as their SimpleBox4Nano model input. Liu and Cohen (2014) used the ENM emission results from Gottschalk et al. (2009) and Keller and Lazareva (2013) as input data for their MendNano fate model. This list exemplifies that the data provided by mass flow models are absolutely crucial for the fate models to come up with correct environmental concentrations as they all rely on mass inputs into one or several environmental compartments. Clearly the to date most reliable and accurate results modelled here by incorporating the true situations of ENM accumulation and release constitute the fundamental input information for realistic concentrations results by environmental fate models.

The concentrations in natural compartments, although based on worst-case assumptions such as no/complete sedimentation or no further dissipation from soils and sediments, provide ecotoxicologists and risk assessors with crucial exposure data needed for first ecological risk assessments. As long as analytical chemists are not able to quantify ENM at the natural concentrations and distinguish them from the natural background particles, the modelled concentrations constitute the only source of environmental exposure information that we have available. The modelled concentrations have previously been used to compare the exposure levels used in toxicological studies Holden et al. (2014) or to perform a full environmental risk assessment based on the comparison of PEC values with NOEC values (no observed effect concentrations) extracted from the ecotoxicological literature Gottschalk et al. (2013a). These assessments rely on the pro-

vision of accurate environmental exposure data and our dynamic modelling is able to provide the most realistic and accurate numbers on flows and accumulated amounts in sinks.

	EU (2014)					
	Mean	**Mode**	Median	$Q_{0.15}$	$Q_{0.85}$	
Nano-TiO_2						
STP Effluent	40.7	8.23	12.9	1.65	67.4	µg/L
STP sludge	1.50	0.493	0.715	0.086	2.98	g/kg
Solid waste to Landfill	12.5	7.41	9.71	4.92	20.1	mg/kg
Solid waste to WIP	10.0	5.9	7.6	3.7	16	mg/kg
WIP bottom ash	372	131	213	76.2	689	mg/kg
WIP fly ash	507	177	280	100	874	mg/kg
Surface water	2.01	0.478	0.953	0.121	4.05	µg/L
Sediment	40.2	26.6	35.7	19.4	62.5	mg/kg
Natural and urban soil	2.13	1.33	1.82	0.969	3.29	µg/kg
Sludge treated soil	57.1	43.6	50.9	26.7	86.8	mg/kg
Air	1.31	0.355	0.574	0.050	2.76	ng/m^3
Nano-ZnO						
STP Effluent	0.000	0.000	0.000	0.000	0.000	µg/L
STP sludge	0.000	0.000	0.000	0.000	0.000	µg/kg
Solid waste to Landfill	1.65	0.962	1.16	0.486	2.39	mg/kg
Solid waste to WIP	1.22	0.677	0.82	0.318	1.85	mg/kg
WIP bottom ash	6.16	2.88	3.95	1.38	9.43	mg/kg
WIP fly ash	11.8	5.20	7.10	2.10	19.5	mg/kg
Surface water	0.337	0.138	0.205	0.026	0.533	µg/L
Sediment	6.56	4.51	5.75	3.38	9.99	mg/kg
Natural and urban soil	1.80	1.05	1.49	0.718	2.94	µg/kg
Sludge treated soil	1.80	1.05	1.49	0.718	2.94	µg/kg
Air	0.845	0.241	0.464	0.051	1.46	ng/m^3
Nano-Ag (1990-2020)						
STP Effluent	1.56	0.443	0.692	0.129	2.84	ng/L
STP sludge	54.9	17.6	24.8	4.29	107	µg/kg
Solid waste to Landfill	82.7	36.8	53.9	20.3	157	µg/kg
Solid waste to WIP	20.6	11.4	14.8	7.31	35.4	µg/kg
WIP bottom ash	173	107	146	78	272	µg/kg
WIP fly ash	337	164	275	109	571	µg/kg
Surface water	1.38	0.497	0.872	0.259	2.71	ng/L
Sediment	26.6	20.2	24.3	15.4	37.8	µg/kg
Natural and urban soil	0.019	0.014	0.018	0.011	0.028	µg/kg
Sludge treated soil	1.98	0.651	1.48	0.333	3.84	µg/kg
Air	0.011	0.005	0.007	0.002	0.021	ng/m^3
Nano-Ag (1900-2020)						
STP Effluent	1.45	0.324	0.624	0.134	2.46	ng/L
STP sludge	51.4	16.7	25.4	4.74	95.2	µg/kg
Solid waste to Landfill	82.3	37.6	54.4	24.8	149	µg/kg
Solid waste to WIP	25.1	15.2	20.2	11.5	40	µg/kg
WIP bottom ash	282	254	265	146	415	µg/kg
WIP fly ash	577	376	480	203	929	µg/kg
Surface water	1.24	0.486	0.773	0.274	2.35	ng/L
Sediment	144	144	142	110	177	µg/kg
Natural and urban soil	0.067	0.059	0.064	0.045	0.088	µg/kg
Sludge treated soil	11.9	3.92	10.50	2.56	21.7	µg/kg
Air	0.010	0.004	0.006	0.002	0.018	ng/m^3
CNT						
STP Effluent	8.58	6.50	7.00	0.93	15.6	ng/L
STP sludge	326	273	277	34.0	593	µg/kg
Solid waste to Landfill	1.26	0.717	1.08	0.542	1.99	mg/kg
Solid waste to WIP	0.99	0.604	0.83	0.419	1.60	mg/kg
WIP bottom ash	0.433	0.170	0.295	0.089	0.79	mg/kg
WIP fly ash	0.92	0.304	0.544	0.145	1.74	mg/kg
Surface water	0.354	0.280	0.295	0.039	0.641	ng/L
Sediment	6.66	6.29	6.38	4.25	9.13	µg/kg
Natural and urban soil	15.8	13.5	15.2	10.2	21.2	ng/kg
Sludge treated soil	11.7	10.2	11.1	7.42	15.8	µg/kg
Air	0.014	0.011	0.012	0.001	0.026	ng/m^3

Table 5.2: Predicted (Accumulated) concentrations of nano-TiO2, nano-ZnO, nano-Ag and CNT in waste streams and environmental compartments in the EU in 2014. Mean, mode, median and 15% and 85% quantiles are shown. Values are rounded to three significant digits. Results for nano-Ag are presented for both the time intervals of the 1900-2020 and 1990-2020 scenarios.

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Author contributions:

B.N. initiated the project and designed the study, analyzed the data and co-wrote the manuscript. K.H. was involved in reviewing the manuscript and provided valuable comments and discussions about the manuscript. N.B. was involved in the modeling work. T.S. performed the modeling work and was involved in planning and conducting the study, and co-wrote the manuscript.

The authors declare no competing financial interests.

Bibliography

Ahmadi, A., Moridi, A., and Han, D. (2015). Uncertainty assessment in environmental risk through bayesian networks. Journal of Environmental Informatics, 25(1).

ATD Home inspection (2014). Average life span of homes, appliances, and mechanicals. *http://www.atdhomeinspection.com/advice/average-product-life/*, Accessed: 2015-06-06.

Baccini, P. and Brunner, P. H. (1991). Metabolism of the anthroposphere. Springer, Berlin, Germany.

Bakas, I., Sieck, M., Hermann, T., Andersen, F. M., and Larsen, H. (2011). Projections of municipal waste management and greenhouse gases. Technical report, European Environment Agency.

Blaser, S. A., Scheringer, M., MacLeod, M., and Hungerbuhler, K. (2008). Estimation of cumulative aquatic exposure and risk due to silver: Contribution of nano-functionalized plastics and textiles. Science of the Total Environment, 390(2-3):396–409.

Bornhöft, N. A. (2015). Dpmfa - a simulation framework for dynamic probablistic material flow analysis. Simulation Package. V. 0.92, *https://pypi.python.org/pypi/dpmfa-simulator*, Accessed: 2015-06-03.

Bornhöft, N. A., Sun, T. Y., Hilty, L. M., and Nowack, B. (2016). A dynamic probabilistic material flow modeling method. Environmental Modelling & Software, 76:69 – 80.

Bornhöft, N. A., Nowack, B., and Hilty, L. M. (2013). Material flow modelling for environmental exposure assessment - a critical review of four approaches using the comparative implementation of an idealized example. In Page, B., Fleischer, A.,

Göbel, J., and Wohlgemuth, V., editors, 27th International Conference on Informatics for Environmental Protection, pages 379–388, Hamburg, Germany. Shaker.

Boxall, A. B. A., Chaudhry, Q., Sinclair, C., Jones, A. D., Aitken, R., Jefferson, B., and Watts, C. (2007). Current and future predicted environmental exposure to engineered nanoparticles. Technical report, Central Science Laboratory, Sand Hutton, UK.

Brunner, P. H. and Rechberger, H. (2004). Practical handbook of material flow analysis. Lewis, Boca Raton.

Bunn, D. W. and Salo, A. A. (1993). Forecasting with scenarios. European Journal of Operational Research, 68(3):291–303.

Caballero-Guzman, A., Sun, T., and Nowack, B. (2015). Flows of engineered nanomaterials through the recycling process in switzerland. Waste Management, 36(0):33–43.

Carlin, B. P. and Louis, T. A. (2000). Bayes and empirical Bayes methods for data analysis. Texts in statistical science series. St. Lucie Press, Boca Raton, Fla, 2nd ed edition. Previous ed.: New York : Chapman & Hall, 1996.

Coll, C., Notter, D., Gottschalk, F., Sun, T., Som, C., and Nowack, B. (2016). Probabilistic environmental risk assessment of five nanomaterials (nano-tio2, nano-ag, nano-zno, cnt, and fullerenes). Nanotoxicology, 10(4):436–44.

Cullen, A. C. and Frey, H. C. (1999). Probabilistic techniques in exposure assessment : a handbook for dealing with variability and uncertainty in models and inputs. Plenum Press, New York [etc.].

Daly, R., Shen, Q., and Aitken, S. (2011). Learning bayesian networks: Approaches and issues. The Knowledge Engineering Review, 26(2)(2):99–157.

Destercke, S., Dubois, D., and Chojnacki, E. (2009). Possibilistic information fusion using maximal coherent subsets. IEEE Transactions on Fuzzy Systems, 17(1):79–92.

Dubois, D. and Prade, H. (2004). On the use of aggregation operations in information fusion processes. Fuzzy Sets and Systems, 142(1):143–161.

Dumont, E., Johnson, A. C., Keller, V. D. J., and Williams, R. J. (2015). Nano silver and nano zinc-oxide in surface waters – exposure estimation for europe at high spatial and temporal resolution. Environmental Pollution, 196(0):341–349.

ECB (2003). Technical guidance document on risk assessment. Technical report, Dublin: European Chemicals Bureau; Institute for Health and Consumer Protection.

ECHA (2012). Guidance on information requirements and chemical safety assessment chapter R.16: Environmental exposure estimation. European Chemicals Agency: Helsinki, Finland, October 2012. p 136.

EEA (2009). EU as a recycling society present recycling levels of municipal waste and construction & demolition waste in the EU. Technical report, European Topic Centre on Sustainable Consumption and Production.

EEA (2012). Movements of waste across the EU's internal and external borders. Technical Report ISSN 1725-9177, European Environment Agency.

EEA Website (2013). Municipal waste recycling rates in 32 european countries, 2001 and 2010. *https://www.eea.europa.eu/data-and-maps/figures/municipal-waste-recycling-rates-in*, Accessed: 2014-11-19.

Erdmann, L. and Hilty, L. M. (2010). Scenario analysis. Journal of Industrial Ecology, 14(5):826–843.

ERPC (2011). European paper recycling rates reach 70.4%. *http://www.regions4recycling.eu/News-and-events/News/european-paper-recycling-rates-reach-70*, Accessed: 2014-11-19.

Forrester, J. W. (1961). Industrial dynamics. The M.I.T. Press, Cambridge, Mass. [u.a.] Productivity Press, Wiley.

Friend of the Earth Europe (2013). Less is more, resource efficiency through waste collection, recycling and reuse of aluminium, cotton and lithium in europe.

Future Markets (2012). Nanomaterials in plastics and advanced polymers. Technical Report 52.

Gamma, E., Helm, R., Johnson, R., and Vlissides, J. (1995). Design Patterns: Elements of Reusable Object-oriented Software. Addison-Wesley Longman Publishing Co., Inc., Boston, MA, USA.

Glass International (2014). Eu glass recycling rate passes 70% mark. *http://www.glass-international.com/news/view/eu-glass-recycling-rate-passes-70-mark*, Accessed: 2014-11-19.

Gondikas, A. P., von der Kammer, F., Reed, R. B., Wagner, S., Ranville, J. F., and Hofmann, T. (2014). Release of tio2 nanoparticles from sunscreens into surface waters: A one-year survey at the old danube recreational lake. Environmental Science & Technology, 48(10):5415–5422.

Gottschalk, F., Kost, E., and Nowack, B. (2013a). Engineered nanomaterials in water and soils: A risk quantification based on probabilistic exposure and effect modeling. Environmental Toxicology and Chemistry, 32(6):1278–1287.

Gottschalk, F., Lassen, C., Kjoelholt, J., Christensen, F., and Nowack, B. (2015). Modeling flows and concentrations of nine engineered nanomaterials in the danish environment. International Journal of Environmental Research and Public Health, 12(5):5581.

Gottschalk, F. and Nowack, B. (2011). Release of engineered nanomaterials to the environment. Journal of Environmental Monitoring, 13:1145 – 1155.

Gottschalk, F., Ort, C., Scholz, R. W., and Nowack, B. (2011). Engineered nanomaterials in rivers – exposure scenarios for switzerland at high spatial and temporal resolution. Environmental Pollution, 159(12):3439–3445.

Gottschalk, F., Scholz, R. W., and Nowack, B. (2010a). Probabilistic material flow modeling for assessing the environmental exposure to compounds: Methodology and an application to engineered nano-TiO2 particles. Environironmental Modelling & Software, 25:320–332.

Gottschalk, F., Sonderer, T., Scholz, R. W., and Nowack, B. (2009). Modeled environmental concentrations of engineered nanomaterials (TiO2, ZnO, Ag, CNT, fullerenes) for different regions. Environmental Science and Technology, 43:9216–9222.

Gottschalk, F., Sonderer, T., Scholz, R. W., and Nowack, B. (2010b). Possibilities and limitations of modeling environmental exposure to engineered nanomaterials by probabilistic material flow analysis. Environmental toxicology and chemistry, 29 5:1036–48.

Gottschalk, F., Sun, T., and Nowack, B. (2013b). Environmental concentrations of engineered nanomaterials: Review of modeling and analytical studies. Environmental Pollution, 181(0):287–300.

Hamby, D. (1994). A review of techniques for parameter sensitivity analysis of environmental models. Environmental Monitoring and Assessment, 32(2):135–154.

Hischier, R., Nowack, B., Gottschalk, F., Hincapie, I., Steinfeldt, M., and Som, C. (2015). Life cycle assessment of façade coating systems containing manufactured nanomaterials. Journal of Nanoparticle Research, 17(2):1–13.

Hoffman, F.O. Gardner, R. (1983). Evaluation of uncertainties in environmental radiological assessment models. In Till, J.E. Meyer, H., editor, Radiological assessments: a textbook on environmental dose assessment, Washington, DC. U.S. Nuclear Regulatory Commission.

Holden, P. A., Klaessig, F., Turco, R. F., Priester, J. H., Rico, C. M., Avila-Arias, H., Mortimer, M., Pacpaco, K., and Gardea-Torresdey, J. L. (2014). Evaluation of exposure concentrations used in assessing manufactured nanomaterial environmental hazards: Are they relevant? Environmental Science and Technology, 48(18):10541–10551.

Hunter, J. D. et al. (2007). Matplotlib: A 2d graphics environment. Computing in Science & Engineering, 9(3)(3):90–95.

Huss, W. R. (1988). Special issue on: The future of forecasting a move toward scenario analysis. International Journal of Forecasting, 4(3):377 – 388.

ifu Hamburg GmbH (2014). Umberto. Computer Program, V. 5.6., *www.umberto.de* Accessed: 2017-12-10.

Johnson, A., Cisowska, I., Jürgens, M., Keller, V., Lawlor, A., and Williams, R. (2011). Exposure assessment for engineered silver nanoparticles throughout the rivers of england and wales (cb0433). Technical report, Centre for Ecology and Hydrology (UK).

Jones, E., Oliphant, T., Peterson, P., et al. (2001). SciPy: Open source scientific tools for Python.

Kaegi, R., Sinnet, B., Zuleeg, S., Hagendorfer, H., Mueller, E., Vonbank, R., Boller, M., and Burkhardt, M. (2010). Release of silver nanoparticles from outdoor facades. Environmental Pollution, 158(9):2900–2905.

Keller, A., McFerran, S., Lazareva, A., and Suh, S. (2013). Global life cycle releases of engineered nanomaterials. Journal of Nanoparticle Research, 15(6):1–17.

Keller, A. A. and Lazareva, A. (2013). Predicted releases of engineered nanomaterials: From global to regional to local. Environmental Science & Technology Letters, 1(1):65–70.

Kiddee, P., Naidu, R., and Wong, M. H. (2013). Electronic waste management approaches: An overview. Waste Management, 33(5):1237–1250.

Klaine, S. J., Koelmans, A. A., Horne, N., Carley, S., Handy, R. D., Kapustka, L., Nowack, B., and von der Kammer, F. (2012). Paradigms to assess the environmental impact of manufactured nanomaterials. Environmental Toxicology and Chemistry, 31(1):3–14.

Kraftfahrt Bundesamt (2003). Pressemitteilung Nr. 30/2003 - Alter Fahrzeugbestand.

Leontief, W. (1986). Input-output economics. Oxford University Press.

Limpiteeprakan, P. (2014). Personal communications.

Liu, H. H. and Cohen, Y. (2014). Multimedia environmental distribution of engineered nanomaterials. Environmental Science & Technology, 48(6):3281–3292.

Lombi, E., Donner, E., Tavakkoli, E., Turney, T. W., Naidu, R., Miller, B. W., and Scheckel, K. G. (2012). Fate of zinc oxide nanoparticles during anaerobic digestion of wastewater and post-treatment processing of sewage sludge. Environmental Science & Technology, 46(16):9089–9096.

Loucks, D., Van Beek, E., Stedinger, J., Dijkman, J., and Villars, M. (2005). Water Resources Systems Planning and Management: An Introduction to Methods, Models and Applications. Studies And Reports in Hydrology. Unesco.

Ma, R., Levard, C., Judy, J. D., Unrine, J. M., Durenkamp, M., Martin, B., Jefferson, B., and Lowry, G. V. (2013). Fate of zinc oxide and silver nanoparticles in a pilot wastewater treatment plant and in processed biosolids. Environmental Science & Technology, 48(1):104–112.

MacLeod, M., Scheringer, M., McKone, T. E., and Hungerbuhler, K. (2010). The state of multimedia mass-balance modeling in environmental science and decision-making. Environ. Sci. Technol., 44(22)(22):8360–8364.

Mahapatra, I., Sun, T. Y., Clark, J. R. A., Dobson, P. J., Hungerbuehler, K., Owen, R., Nowack, B., and Lead, J. (2015). Probabilistic modelling of prospective environmental concentrations of gold nanoparticles from medical applications as a basis for risk assessment. Journal of Nanobiotechnology, 13(1):93.

McKay, M. D., Beckman, R. J., and Conover, W. J. (1979). Comparison of three methods for selecting values of input variables in the analysis of output from a computer code. Technometrics, 21(2):239–245.

McKinney, W. (2014). pandas: a python data analysis library. V. 0.15.1., *http://pandas.pydata.org/*, Accessed: 2014-12-01.

Meesters, J. A. J., Koelmans, A. A., Quik, J. T. K., Hendriks, A. J., and van de Meent, D. (2014). Multimedia modeling of engineered nanoparticles with simplebox4nano: Model definition and evaluation. Environmental Science & Technology, 48(10):5726–5736.

Mitrano, D. M., Lesher, E. K., Bednar, A., Monserud, J., Higgins, C. P., and Ranville, J. F. (2012). Detecting nanoparticulate silver using single-particle inductively coupled plasma-mass spectrometry. Environmental Toxicology and Chemistry, 31(1):115–121.

Mitrano, D. M., Motellier, S., Clavaguera, S., and Nowack, B. (2015). Review of nanomaterial aging and transformations through the life cycle of nano-enhanced products. Environment International, 77(0):132–147.

Möller, A. (2000). Grundlagen stoffstrombasierter betrieblicher Umweltinformationssysteme. Projekt-Verl., Bochum.

Money, E. S., Reckhow, K. H., and Wiesner, M. R. (2012). The use of bayesian networks for nanoparticle risk forecasting: Model formulation and baseline evaluation. Science of the Total Environment, 426(0)(0):436–445.

Morrison, F. (1991). The art of modeling dynamic systems : forecasting for chaos, randomness, and determinism. Wiley, New York.

Mueller, N. C. and Nowack, B. (2008). Exposure modeling of engineered nanoparticles in the environment. Environmental Science and Technology, 42:4447–4453.

Müller, E., Hilty, L. M., Widmer, R., Schluep, M., and Faulstich, M. (2014). Modeling metal stocks and flows: A review of dynamic material flow analysis methods. Environmental Science & Technology, 48(4)(4):2102–2113.

Nowack, B., Baalousha, M., Bornhoft, N., Chaudhry, Q., Cornelis, G., Cotterill, J., Gondikas, A., Hassellov, M., Lead, J., Mitrano, D. M., von der Kammer, F., and Wontner-Smith, T. (2015). Progress towards the validation of modeled environmental

concentrations of engineered nanomaterials by analytical measurements. Environental Science: Nano, 2:421–428.

Nowack, B., Krug, H. F., and Height, M. (2011). 120 years of nanosilver history: implications for policy makers. Environtal Science and Technology, 45:1177–1183.

Page, B. and Kreutzer, W. (2005). The Java simulation handbook : simulating discrete event systems with UML and Java. Shaker, Aachen, Germany.

Pate-Cornell, M. E. (1996). Uncertainties in risk analysis: Six levels of treatment. Reliability Engineering and System Safety, 54(2-3):95–111.

Pearl, J. (1985). Bayesian networks: A model of self-activated memory for evidential reasoning proceedings of the 7th conference of the cognitive science society. In Proceedings of the 7th Conference of the Cognitive Science Society, pages 329–334.

Peterson, J. L. (1981). Petri net theory and the modeling of systems. Prentice-Hall, Englewood Cliffs, NJ.

Piccinno, F., Gottschalk, F., Seeger, S., and Nowack, B. (2012). Industrial production quantities and uses of ten engineered nanomaterials in europe and the world. Journal of Nanoparticle Research, 14(9)(9):1–11.

Praetorius, A., Scheringer, M., and Hungerbühler, K. (2012). Development of environmental fate models for engineered nanoparticles - a case study of tio2 nanoparticles in the rhine river. Environmental Science & Technology, 46(12):6705–6713.

Python Software Foundation (2014). Python language reference. V. 2.7., *http://www.python.org*, Accessed: 2014-08-07.

R Development Core Team (2012). R: A language and environment for statistical computing. *http://www.R-project.org*, Accessed: 2017-12-10.

Refsgaard, J. C., van der Sluijs, J. P., Højberg, A. L., and Vanrolleghem, P. A. (2007). Uncertainty in the environmental modelling process - a framework and guidance. Environmental Modelling and Software, 22(11):1543–1556.

Restrepo, E. (2015). Personal communication.

Saltelli, A., Ratto, M., Andres, T., Campolongo, F., Cariboni, J., Gatelli, D., Saisana, M., and Tarantola, S. (2008). Introduction to Sensitivity Analysis, pages 1–51. John Wiley & Sons, Ltd.

Savolainen, K., Alenius, H., Norppa, H., Pylkkänen, L., Tuomi, T., and Kasper, G. (2010). Risk assessment of engineered nanomaterials and nanotechnologies - a review. Toxicology, 269(2 - 3):92 – 104.

Scott, D. W. (1992). Multivariate density estimation: theory, practice, and visualization. Wiley series in probability and mathematical statistics. Wiley, New York.

Smets, P. (2005). Belief functions on real numbers. International Journal of Approximate Reasoning, 40(3):181 – 223.

Smets, P. (2007). Analyzing the combination of conflicting belief functions. Information Fusion, 8(4):387–412.

Streicher-Porte, M. (2014). Ab ins recycling – aber wann? In Fachbericht 2014, pages 17–18. Stiftung Entsorgung Schweiz, Swico and Stiftung Licht Recycling Schweiz.

Sun, T. Y., Bornhöft, N. A., Hungerbühler, K., and Nowack, B. (2016). Dynamic probabilistic modeling of environmental emissions of engineered nanomaterials. Environmental Science & Technology, 50(9):4701–4711.

Sun, T. Y., Conroy, G., Donner, E., Hungerbuhler, K., Lombi, E., and Nowack, B. (2015). Probabilistic modelling of engineered nanomaterial emissions to the environment: a spatio-temporal approach. Environmental Science: Nano.

Sun, T. Y., Gottschalk, F., Hungerbühler, K., and Nowack, B. (2014). Comprehensive probabilistic modelling of environmental emissions of engineered nanomaterials. Environmental Pollution, 185(0):69–76.

Sun, T. Y., Mitrano, D. M., Bornhöft, N. A., Scheringer, M., Hungerbühler, K., and Nowack, B. (2017). Envisioning nano release dynamics in a changing world: Using dynamic probabilistic modeling to assess future environmental emissions of engineered nanomaterials. Environmental Science & Technology, 51(5):2854–2863.

TU Vienna, Institute for Water Quality, Resource and Waste Management (2012). STAN, subSTance flow ANalysis. V. 2.5., *http://www.stan2web.net/* Accessed: 2014-09-05.

van der Walt, S., Colbert, S. C., and Varoquaux, G. (2011). The numpy array: A structure for efficient numerical computation. Computing in Science & Engineering, 13(2)(2):22–30.

von der Kammer, F., Ferguson, P. L., Holden, P. A., Masion, A., Rogers, K. R., Klaine, S. J., Koelmans, A. A., Horne, N., and Unrine, J. M. (2012). Analysis of engineered nanomaterials in complex matrices (environment and biota): General considerations and conceptual case studies. Environmental Toxicology and Chemistry, 31(1):32–49.

Walser, T. and Gottschalk, F. (2014). Stochastic fate analysis of engineered nanoparticles in incineration plants. Journal of Cleaner Production, 80:241 – 251.

Wick, P., Clift, M. J. D., Rösslein, M., and Rothen-Rutishauser, B. (2011). A brief summary of carbon nanotubes science and technology: A health and safety perspective. ChemSusChem, 4(7):905–911.

Wohlgemuth, V. (2005). Komponentenbasierte Unterstützung von Methoden der Modellbildung und Simulation im Einsatzkontext des betrieblichen Umweltschutzes: Konzeption und prototypische Entwicklung eines Stoffstromsimulators zur Integration einer stoffstromorientierten Perspektive in die auftragsbezogene Simulationssicht. Shaker, Aachen.

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Part III.

Appendix

A

Tutorial of the Simulation Framework

The dynamic probabilistic material flow method, described in this thesis (chapter 3), and applied in the case studies of chapter 3, 4, and the simulation study (chapter 5) is provided as simulation package in Python. It can be retrieved from *PyPI - the Python Package Index*: *https://pypi.python.org/pypi/dpmfa-simulator*.

The dpmfa framework supports the generation and use of dynamic probabilistic material flow models. It enables to model time dynamic flow models on a period basis. Incomplete knowledge about the true values of a system parameter about the absolute inflows to the system over time and the relative transfer coefficients for the flows between the system compartments is represented as a (Bayesian) probability distribution. This parameter distributions needs to be chosen in a way that it includes all plausible values and assign respective likelihoods. The assumptions represented in these parameter distributions are propagated to the dependent model variables using Monte-Carlo simulation while ensuring mass-balance in every element of the sample.

The `dpmfa_simulator` package holds a simulation infrastructure providing a ready-to-use simulator class and a set of components that are used to implement system specific entities and assemble them as a model. Also, an example package is included, which contains a small example model and a runner file to illustrate the use of the dpmfa simulator.

The simulation package comes with an extensive documentation and an explanatory example to illustrate the modeling and evaluation process, which is presented in the following. I recommend to use an integrated modelling environment (IDE), such as Spyder[1] to support the model development.

[1] *https://github.com/spyder-ide/spyder*, last accessed 2015-11-18

A.1. Example system

The example consists of an model, which represents the structure and a behaviour of a specific system of dependent stocks and flows. Performing simulation experiments with the model allows drawing conclusions about the original system. In particular, the state of dependent material stocks over time can be reproduced and investigated over time, including the inherent parameter uncertainty.

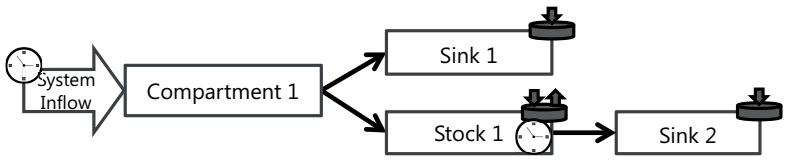


Figure A.1: Structure of the example model

The example model has the following characteristics:

- The model includes a material inflow source to flow compartment “Flow Compartment 1” where the flow is split into a part that is transferred to the sink compartment “Sink 1” and the stock compartment “Stock 1”. After a delay, the inflow to “Stock 1” is further transported to “Sink 2”(figure A.1).
- The model parameters for the absolute input to the system and the relative transfer coefficients in the split of the flow in “Compartment 1” are assumed to be not precisely known.
- The model inflow is represented by an independent normal distribution for each period. In the first period a mean value of 1000 t is assumed, increased by 200 t in every subsequent period. For each distribution the standard deviation is 250 t.
- At the split in “Compartment 1” the proportion that is further transferred to “Sink 1” is defined as triangular distribution with a mode value of 0.7 and a minimum value of 0.5 and a maximum value of 0.9. (This way incomplete knowledge about the true value is expressed. The range between 0.5 and 0.9 is considered plausible and the mode of 0.7 is assumed to be the most likely value.) The remainder from that flow is transferred to “Stock 1”.
- The inflow to “Stock 1” is kept there for a delay of 2 periods. In each of the following 2 periods 50 % of the material is further transported to “Sink 2”.
- The Sinks 1 and 2 mark the endpoints of the material streams.

It is simulated over a time horizon of 5 periods (e.g. representing 5 years) and a sample size of 200. For each single simulation run from the sample for all parameters random values are drawn from the respective probability distributions. For each of these particular particular parameter settings the development of stocks and flows is calculated through out the simulation process. The simulation results for the variables under examination such as stocks and flow volumes are provided as matrix of values over time and sample size. Based on these matrices further evaluations and visualizations can be performed. Listing A.1 shows the implementation of the example model.

Listing A.1: Example Model

```
# the numpy.random package is imported to use probability distribution functions;
    the components are used to implement system specific behaviour and assembled
    to a model.
import numpy.random as nr
import dpmfa_simulator.components as cp
import dpmfa_simulator.model as model

# creation of the Model
exampleModel = model.Model('Example Model')

# creation of the Flow Compartment
compartment1 = cp.FlowCompartment('Flow Compartment 1', logInflows = True,
    logOutflows =True)

# creation of the Stock
stock1 = cp.Stock('Stock 1', logInflows = True, logOutflows = True)

# Sinks
sink1 = cp.Sink('Sink 1', logInflows = True)
sink2 = cp.Sink('Sink 2', logInflows = True)


# the external inflows to the system are defined as a list, of independent normal
    distributions for each period.
inflow = cp.ExternalListInflow(compartment1, [\
    cp.StochasticFunctionInflow(nr.normal, [1000, 250]),
    cp.StochasticFunctionInflow(nr.normal, [1200, 250]),
    cp.StochasticFunctionInflow(nr.normal, [1400, 250]),
    cp.StochasticFunctionInflow(nr.normal, [1600, 250]),
    cp.StochasticFunctionInflow(nr.normal, [1800, 250])])


# material transfer from the flow compartment to Sink 1 as triangular distribution
# The remaining part transferred to Stock 1.
compartment1.transfers = [cp.StochasticTransfer(nr.triangular, [0.5, 0.7, 0.9],
    sink1, priority = 2),
                          cp.ConstTransfer(1, stock1, priority = 1)]
```

```
    # release strategy, defining the delay time and the release rates based on
        material transferred to Stock 1
    stock1.localRelease = cp.ListRelease([0.5, 0.5], delay = 2)
36
    # total release from Stock in transferred to Sink 2
    stock1.transfers = [cp.ConstTransfer(1, sink2)]

    # add compartments and inflow to the model
41  exampleModel.setCompartments([compartment1, stock1, sink1, sink2])
    exampleModel.setInflows([inflow])
```

A.2. Simulation and Evaluation

In the example runner (listing A.2) a simulator object is instantiated and parametrised. Then the example model (listing A.1) is connected to it and the simulation process is performed. Subsequently, the accumulated material in stocks and sinks over time is printed to console and plotted to allow a detailed representation and visualization of the results.

Listing A.2: Example Runner

```
    # The simulator package and the example model are imported to instantiate a
        simulator and perform the model evaluation with it. The packages numpy for
        numerical Python and matplotlib are needed for statistical evaluations and
        plotting the results.
 2  import dpmfa_simulator.simulator as sc
    import example.example_model
    import numpy as np
    import matplotlib.pyplot as plt

 7  # the example model
    model = example.example_model.exampleModel
    model.checkModelValidity()

    # investigated number of periods (e.g. Years in the original system)
12  PERIODS = 5

    # For each element of the sample the model is calculated once using a set of
        random values for the model parameters from the underlying probability
        distributions.
    SAMPLESIZE = 200

17  # create the simulator
    simulator = sc.Simulator(SAMPLESIZE, PERIODS, 1, True, True)

    # connect the model
    simulator.setModel(model)
```

```
22
# The Monte-Carlo simulation process is performed.
simulator.runSimulation()

#============================================================================
#  Evaluation of the simulation results.
#
#  Display the material amount in sinks and stocks over time:
#   - by printing the inventory matrix
#   - plotting the simulation output as series of annual values for each sample (
    grey lines)
32 #   - calculating the annual mean values (red line)
#============================================================================

# the model sinks/stocks
sinks = simulator.getSinks()
37
# plotting / evaluation of all model stocks
allFigures = []
figureNumber = 0
xRange = np.arange(PERIODS)
42
for sink in sinks:
    print ''
    print sink.name + ':'
    print sink.inventory
47  fig = plt.figure(figureNumber)
    figureNumber +=1
    plt.title(sink.name)
    plt.xlabel('Period')
    plt.ylabel('Amount in tons')
52
    sinkInv = sink.inventory

# plot time series of the whole sample
    for row in sinkInv:
57      plt.plot(xRange, row, color = '0.5', lw = 1)

# add the time series of the mean values of the sample
    sinkMeans = []
    for row in sink.inventory.transpose():
62      sinkMeans.append(np.mean(row))
    plt.plot(xRange, sinkMeans, color = 'red', linewidth=2)
```

The simulation results as the inventories of “Stock 1”, “Sink 1”, and “Sink 2” over time are plotted to console (listing A.2, line 43-46). The output (listing A.3) shows the unprocessed data of the inventories as 2-dimensional arrays. Each of the lines shows a time series under one particular set of parameter values. A row displays the values at a specific time period over the random sample. The results are visualized in the Figures

A.2,A.3 and A.4. The grey lines in the displays display the time series of the material amount for a random parameter set. The red line shows the time series of mean values over the entire sample.

Listing A.3: Console output:

```
1
  Start Simulation
  Model: Example Model
  Seed Value: 1
  Number of Simulation Runs: 200
6 Number of Periods: 5
  Progress (in percent):
  1,
  Simulation complete


11
  Stock 1:
  [[  253.70599759   598.9109573    828.60356502   905.6405703    938.48115442]
   [  332.11531405   663.17606301   843.1566795   1020.03035207  1013.88808257]
  ...
16 [  286.51027805   557.72404123   908.94675851  1165.38834446  1347.23770279]
   [  363.62208192  1028.63674703  1468.17750098  1710.95769612  1999.74969181]]

  Sink 1:
  [[  545.75079275  1288.32638111  2055.2970056   2865.17565856  3690.59264013]
21 [  951.72102292  1900.42004798  2892.03918059  4349.10446078  5301.66204167]
  ...
   [  690.4963972   1344.12783972  2535.83091087  3825.92498445  5186.85340111]
   [  423.86482378  1199.0551597   1923.34882101  2805.87897344  3892.25830638]]

26 Sink 2:
  [[    0.            0.          126.85299879   426.30847744   777.18376055]
   [    0.            0.          166.05765703   497.64568853   836.19519977]
   ...
   [    0.            0.          143.25513903   422.11715964   804.96296938]
31 [    0.            0.          181.81104096   696.12941448  1339.31264448]]
```

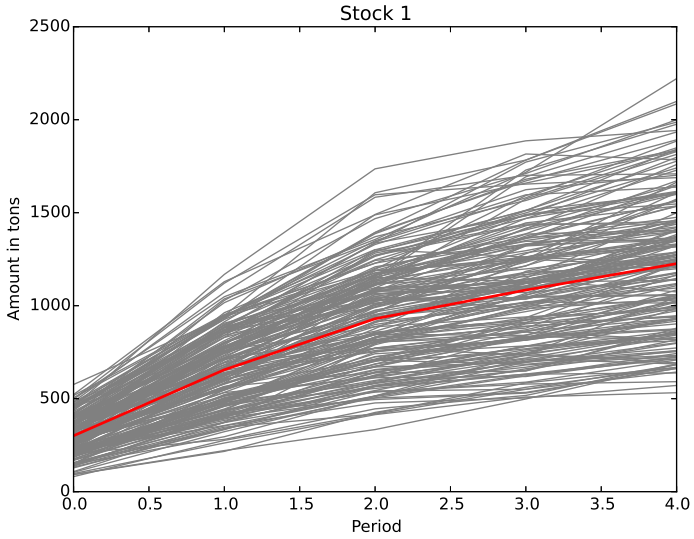


Figure A.2: Material in Stock 1 of the Example Model over Time

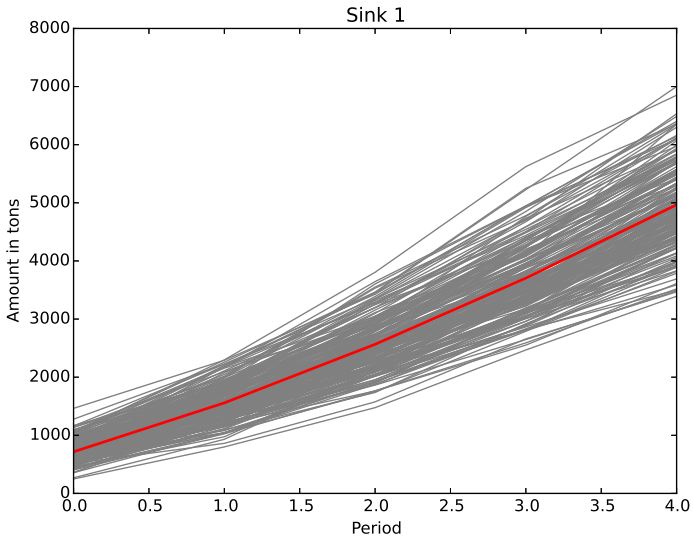


Figure A.3: Material in Sink 1 of the Example Model over Time

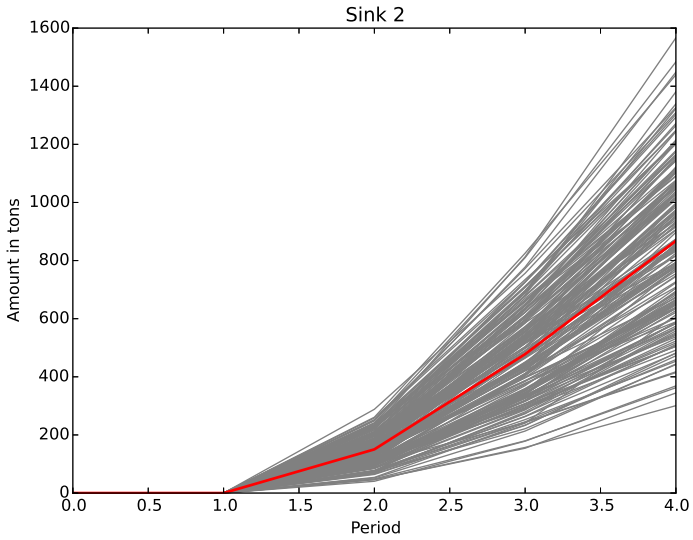


Figure A.4: Material in Sink 2 of the Example Model over Time

B

Supplementary Information: Chapter 3

B.1. Model

The CNT case study model is shown in more detail, describing its model structure and parameterization as well as the results of the sensitivity and uncertainty analyzes.

B.1.1. Flow Compartments:

Total system inflow, CNT production, manufacture, consumption, paint, textiles, energy, sensors, aerospace, waste incineration plant (WIP), WIP ashes, WIP filter, WIP solid ash, WIP filter wet scrubber, WIP acid washing, sewage treatment plant (STP), STP treated, surface water, waste water, sewage sludge, air, soil

B.1.2. Model Stocks:

Polymer composites, consumer electronics, automotive

B.1.3. Model Sinks:

Elimination, recycling, export, cement plant, landfill, sediment, soil sink

B.1.4. Transfer Coefficients:

Table B.1: Parametrization of all TCs of the Case-Study model

From	**To**	**Rate/Parameter Distribution**
Total Inflow	Production	Deterministic 0.005
	Manufacture	Deterministic 0.005
	Consumption	Deterministic 0.99
Production	Waste Water	TriangularDist[1] (0.61, 0.74, 0.87)
	Air	TriangularDist (0.13, 0.24, 0.39)
Manufacture	Waste Water	TriangularDist (0.165, 0.33, 0.495)
	Waste Incineration	TriangularDist (0.165, 0.33, 0.495)
	Air	TriangularDist (0.175, 0.35, 0.525)
Consumption[2]	Polymer Composites	TriangularDist (0.25, 0.84, 1)
	Paints	TriangularDist (0.00, 0.014, 0.1)
	Textiles	TriangularDist (0.000, 0.0002, 0.0007)
	Automotive	TriangularDist (0.00, 0.013, 0.1)
	Consumer Electronics	TriangularDist (0.0, 0.031, 0.24)
	Energy	TriangularDist (0.0, 0.091, 0.5)
	Sensor	TriangularDist (0.00, 0.004, 0.03)
	Aerospace	TriangularDist (0.00, 0.006, 0.05)
Polymer Composites	Waste Incineration	TriangularDist (0.982, 0.988, 0.994)
	Air	TriangularDist (0.006, 0.012, 0.018)
Paints	Waste Water	TriangularDist (0.005, 0.01, 0.015)
	Landfill	TriangularDist (0.25, 0.5, 0.75)
	Air	TriangularDist (0.005, 0.01, 0.015)
	Soil	TriangularDist (0.005, 0.01, 0.015)
	Surface Water	TriangularDist (0.005, 0.01, 0.015)
	Recycling	TriangularDist (0.23, 0.46, 0.69)
Textiles	Waste Water	TriangularDist (0.01, 0.02, 0.03)
	Waste Incinearation	TriangularDist (0.48, 0.96, 1)
	Air	TriangularDist (0.01, 0.02, 0.03)
Automotive	Waste Incinearation	TriangularDist (0.195, 0.39, 0.585)
	Air	TriangularDist (0.005, 0.01, 0.015)
	Recycling	TriangularDist (0.2, 0.4, 0.6)
	Export	TriangularDist (0.1, 0.2, 0.3)
Consumer Electronics	Waste Incinearation	TriangularDist (0.025, 0.05, 0.075)
	Recycling	TriangularDist (0.375, 0.75, 1)
	Export	TriangularDist (0.1, 0.2, 0.3)
Energy	Waste Incinearation	TriangularDist (0.025, 0.05, 0.075)

[1]Triangular Distribution (min, mode, max)

[2]The material distribution of "Consumption" to different product categories does not exclusively use symmetric triangular distributions. Therefore, it is not included in the model robustness considerations of section 4.3.3.

	Recycling	TriangularDist (0.375, 0.75, 1)
	Export	TriangularDist (0.1, 0.2, 0.3)
Sensor	Waste Incinearation	TriangularDist (0.025, 0.05, 0.075)
	Recycling	TriangularDist (0.375, 0.75, 1)
	Export	TriangularDist (0.1, 0.2, 0.3)
Aerospace	Waste Incinearation	TriangularDist (0.195, 0.39, 0.585)
	Air	TriangularDist (0.005, 0.01, 0.015)
	Recycling	TriangularDist (0.3, 0.6, 0.9)
Waste Water	Surface Water	UniformDist[3] (0.032, 0.004)
	STP[4]	1 - (Waste Water ->Surface Water)
STP	Surface Water	NormalDist[5] (0.032, 0.004)
	STP Treatment	1 - (STP ->Surface Water)
STP Treatment	Sewage Sludge	Combined Weighted Distribution:
		1/6,->TriangularDist (0.83, 0.88, 0.93)
		1/6,->TriangularDist (0.895, 0.93, 0.965)
		1/6,->TriangularDist (0.925, 0.95, 0.975)
		1/2,->UniformDist (0, 1)
	Surface Water	1 - (STP Treatment ->Sewage Sludge)
Sewage Sludge	Waste Incineration	Deterministic 0.78
	Cement Plant	Deterministic 0.22
Waste Incineration	Elimination	TriangularDist (0.75, 0.98, 1)
	WIP[6] Ashes	1 - (Waste Incineration ->Elimination)
WIP Ashes	Landfill	TriangularDist (0.4, 0.81, 1)
	WIP Filter	1 - (WIP Ashes ->Landfill)
WIP Filter	WIP Filter Solid Ash	UniformDist (0.995, 0.999)
	WIP Filter Wet Scrubber	1 - (WIP Filter ->WIP Filter Solid Ash)
WIP Filter Solid Ash	Landfill	Deterministic 0.78
	Export	Deterministic 0.22
WIP Filter Wet Scrubber	Air	TriangularDist (0.0005, 0.001, 0.0015)
	Landfill	1 - (WIP Filter Wet Scrubber ->Air)
Air	Surface Water	Deterministic 0.03
	Soil	Deterministic 0.97
Soil	Surface Water	TriangularDist (0.003, 0.00549, 0.008)
	Soil Sink	1 - (Soil ->Surface Water)
Surface Water	Sediment	Deterministic 1

[3]Uniform Distribution (min, max)
[4]STP = Sewage Treatment Plant
[5]Normal Distribution (mean, standard deviation)
[6]WIP = Waste Incineration Plant

B.1.5. Delay Functions

Table B.2: Annual material release rates from the model stocks starting from the material storage time

Stock	**Delay Function**
Polymer Composites	NormalDist (mean = 7 y, sd = 3 y)
Consumer Electronics	Release list annual rates for the following years: [0.011, 0.019, 0.033, 0.061, 0.083, 0.11, 0.107, 0.145, 0.113, 0.078, 0.067, 0.072, 0.033, 0.024, 0.018, 0.008, 0.006, 0, 0, 0.005, 0.003,
Automotive	NormalDist (mean = 12.9 y, sd = 5 y)

B.1.6. Production Volumes: Scaling factors

Table B.3: Annual scaling factor of the basic production volume

Year	**Factor**
2003	0.0
2004	0.0672
2005	0.1294
2006	0.2015
2007	0.3164
2008	0.3359
2009	0.6718
2010	0.6982
2011	0.8525
2012	1.0
2013	1.2016
2014	1.3963
2015	1.6046
2016	1.8264
2017	2.0617
2018	2.3105
2019	2.5728
2020	2.8487

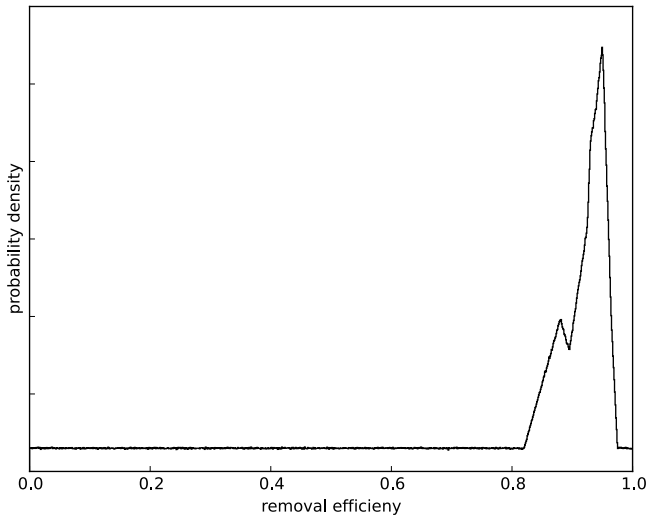


Figure B.1: CNT removal efficiency in sewage treatment plants (STP)

B.2. Sensitivity Analysis

Table B.4: Sensitivity analysis, correlation of relative parameter changes and relative changes of model variables for the environmental sinks soils and sediments for the year 2012 and 2020 (mean values).

Parameter	Sediment 2012	Soil 2012	Sediment 2012	Soil 2012
Basic Scenario (tons)	*0.1774*	*0.3501*	*0.8523*	*2.1376*
Annual Prod. +1%	1.0147	0.9997	0.9973	1.0011
STPtreat ->Surface Water	0.6505	0.0000	0.6367	0.0000
Tot. Inflow ->Product.	0.5293	0.2622	0.5182	0.2009
Product. ->WasteW	0.4577	-0.7572	0.4482	-0.5832
Tot. Inflow ->Manuf.	0.2480	0.3513	0.2429	0.2695
Manuf. ->wastW	0.2136	-0.1722	0.2094	-0.1325
Consumpt ->paints	0.1979	0.1348	0.1927	0.0956
Paints ->SurfaceW	0.1437	-0.0014	0.1410	-0.0011
Air ->SurfaceWater	0.0564	-0.0288	0.0732	-0.0292
STP ->Surface Water	0.0524	0.0000	0.0516	0.0000
Paints ->WastW	0.0462	-0.0014	0.0454	-0.0011
WasteW ->SurfaceW	0.0434	0.0000	0.0425	0.0000

Composites ->Air	0.0141	0.1971	0.0346	0.3766
Soil ->surfaceWater	0.0107	-0.0057	0.0140	-0.0055
Paints ->Air	0.0034	0.0697	0.0032	0.0538
Aerospace ->Air	0.0028	0.0346	0.0025	0.0268
Consumpt.->textiles	0.0011	0.0011	0.0009	0.0009
Textiles ->WastW	0.0011	0.0000	0.0009	0.0000
Automotive ->Air	0.0000	0.0029	0.0007	0.0071
Textiles ->Air	0.0000	0.0011	0.0001	0.0010
Electronics - >WIP	0.0000	0.0000	0.0000	0.0000
Elect. ->Recycling	0.0000	0.0000	0.0000	0.0000
Elect. ->Export	0.0000	0.0000	0.0000	0.0000
Energy ->WIP	0.0000	0.0000	0.0000	0.0000
Energy ->Recycling	0.0000	0.0000	0.0000	0.0000
Energy ->Export	0.0000	0.0000	0.0000	0.0000
Sensors ->WIP	0.0000	0.0000	0.0000	0.0000
Sensors ->Recycling	0.0000	0.0000	0.0000	0.0000
Sensors ->Export	0.0000	0.0000	0.0000	0.0000
SewSludge ->Cement	0.0000	0.0000	0.0000	0.0000
WIP ->Elimination	0.0000	0.0000	0.0000	0.0000
WIPAshes ->landfill	0.0000	0.0000	0.0000	0.0000
SolidAsh ->landfill	0.0000	0.0000	0.0000	0.0000
SolidAsh ->Export	0.0000	0.0000	0.0000	0.0000
WetScrubber ->Air	0.0000	0.0000	0.0000	0.0000
WIPFilter ->SolidAsh	0.0000	-0.0006	0.0000	-0.0008
Automotive ->Export	0.0000	-0.0009	-0.0001	-0.0018
Automotive ->WIP	0.0000	-0.0020	-0.0004	-0.0045
Automotive ->Recycling	0.0000	-0.0020	-0.0004	-0.0047
Paints ->Soil	-0.0011	0.0720	-0.0012	0.0555
Consumpt. ->Aerospace	-0.0011	0.0286	-0.0015	0.0182
Aerospace ->WIP	-0.0017	-0.0223	-0.0015	-0.0171
Consumpt. ->Sensors	-0.0023	-0.0040	-0.0023	-0.0055
Aerospace ->Recycling	-0.0039	-0.0523	-0.0036	-0.0401
Consumpt. ->Automotive	-0.0073	-0.0109	-0.0077	-0.0116
Textiles ->WIP	-0.0203	-0.0271	-0.0198	-0.0208
Consumpt. ->Electronics	-0.0192	-0.0343	-0.0209	-0.0470
Consumpt. ->Energy	-0.0474	-0.0837	-0.0513	-0.1150

Manuf. ->Air	-0.0941	0.3545	-0.0923	0.2731
Manuf. ->WIP	-0.1223	-0.1722	-0.1197	-0.1325
Prod. ->Air	-0.1607	0.2659	-0.1575	0.2049
Paints ->Recycling	-0.1691	-0.1223	-0.1652	-0.0941
Paints ->Landfill	-0.1984	-0.1437	-0.1941	-0.1105
Consumpt. ->Composites	-0.3439	-0.1265	-0.3166	0.1190
STP ->STPtreat	-1.5924	0.0000	-1.5587	0.0000
STPtreat ->Sewage Sludge	-1.5924	0.0000	-1.5587	0.0000
Air ->Soil	-1.8298	0.9272	-2.3672	0.9439
Composites ->WIP	-1.1731	-16.2265	-2.8489	-31.0108
Tot. Inflow ->Consump.	-77.3754	-61.0557	-75.7216	-46.7995

B.3. Uncertainty Analysis

Table B.5: Uncertainty analysis: calculation of the influence of the uncertainty ranges of the model parameters on the uncertainty of the model output on the example of the sediment stock in 2020. The relative parameter range refers to the expected mean as base. The model parameters are ordered by the relative impact on the uncertainty about the model output. Deterministic parameters and parameters that only provide a very small contribution are not considered in the list.

Parameter	min Value	max Value	Sediment 2020 (min)	Sediment 2020 (max)	uncertainty range	relative range (%)
Input: Production	Annual values		0.0246	2.07	2.0455	240%
TC: STP treatment ->surface water	0.1	0.97	1.9937	0.3658	1.6279	191%
TC: consumption ->paints	0	0.1	0.6881	1.159	0.4709	55%
TC: consumpt. ->composites	0.25	1	1.0166	0.7	0.3166	37%
TC: manufacture ->waste water	0.165	0.495	0.7639	0.9442	0.1803	21%
TC: paints ->landfill	0.25	0.75	0.935	0.7696	0.1654	19%
TC: paints ->recycling	0.23	0.69	0.9227	0.7818	0.1409	17%
TC: production ->waste water	0.61	0.87	0.7852	0.9194	0.1342	16%
TC: paints ->surface water	0.005	0.015	0.7922	0.9123	0.1201	14%
TC: manufacture ->WIP	0.165	0.495	0.9028	0.7997	0.1031	12%
TC: manufacture ->air	0.175	0.525	0.8912	0.8117	0.0795	9%
TC: composites ->WIP	0.982	0.994	0.867	0.8375	0.0295	3%
TC: waste water ->surface water	0.02	0.033	0.8434	0.8611	0.0177	2%

C

Supplementary Information: Chapter 4

C.1. Input dynamics

The estimation of the development of ENM production over time is made by multiplying the base year's (2012) production with the scaling factors of the other years. The production distribution of five ENM in 2012 is given in Sun et al.1. This forms the basis of the updated production distribution of nano-TiO_2, nano-ZnO, nano-Ag and CNT in 2012 used in this study. Table S1 shows the raw data of ENM production volume reported which are used for building the probability distribution. The figures in black are taken from the study by Sun et al. (2014), and the figures in red are new data found after that study. These figures are subjectively assigned a degree of belief (DoB) based on the reliability and degree of depth the cited source acquired the figures which hinges on how precisely the author collected information to arrive at the given figures. To cover the unknown uncertainty of these data, a single number is deviated by 50% and factor 2 to have a triangular distribution; for data in a range, a uniform distribution is built. Finally these individual distributions based on the data from different sources are combined to represent the compiled knowledge of all information. The scaling factors for each individual years are based on ENM market projections, nanotechnology patent analysis, and the direct ENM production projection (Piccinno et al., 2012) when available. Data for general nanotechnology are used for all the four ENM studied; there are also data especially for CNT. A second reference year is made in 2005 for the data that do not reach to 2012, so that all the data can be compared to the year 2012. A summary of all the data used for estimating the scaling factors is given in Table S2. These variable scaling factors for each individual year are used for building a normal distribution. Once both the updated ENM production distribution of 2012 and the distribution of scaling factors are given, they are multiplied to get the production distribution of the years retrospective and prospective.

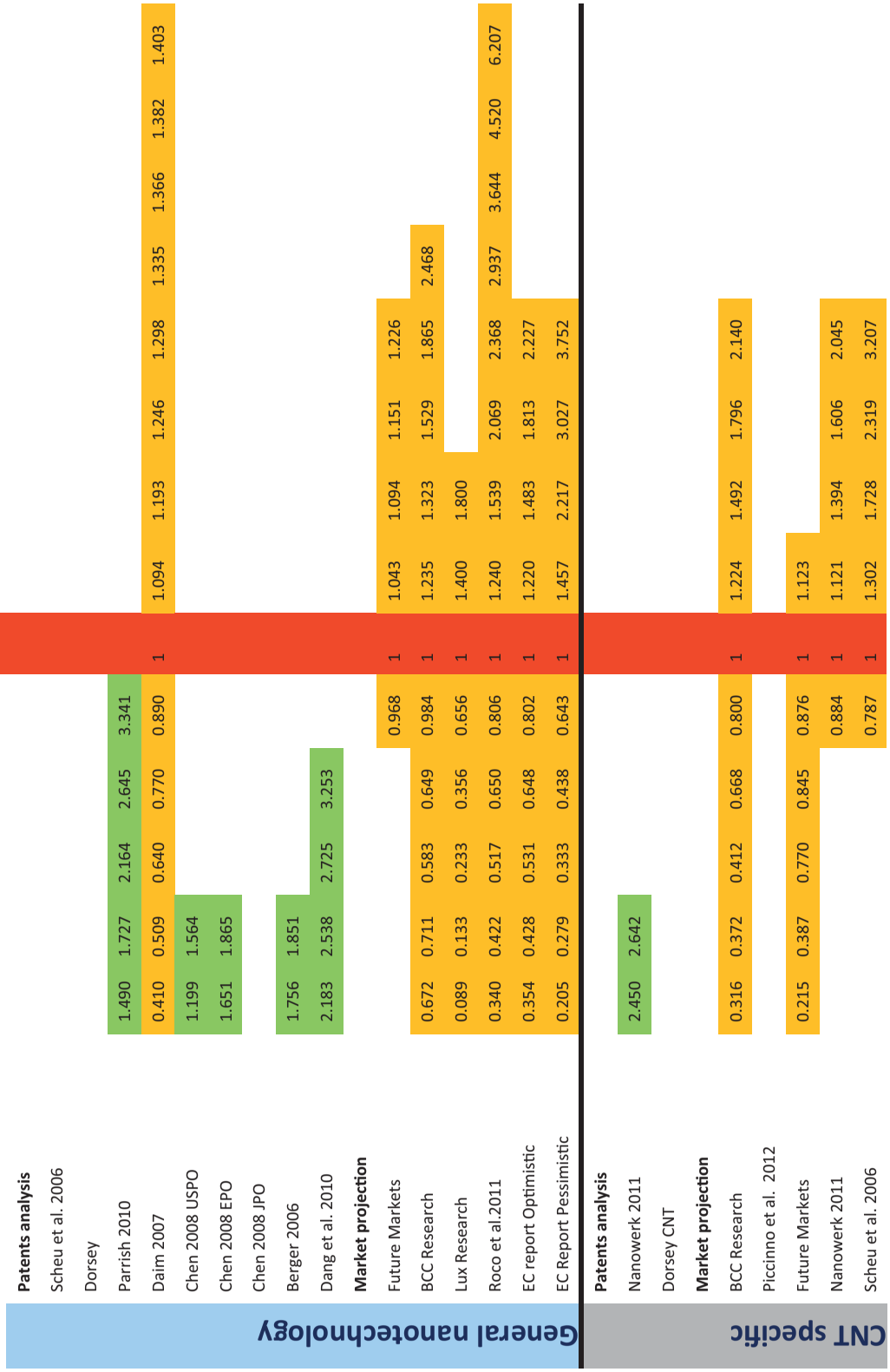
[1]Migros (2012)
[2]EPA, US Environmental Protection Agency (2010)
[3]Piccinno et al. (2012)
[4]Robichaud et al. (2009)
[5]Hendren et al. (2011)
[6]Nightingale et al. (2008)
[7]Schmid and Riediker (2008)
[8]Keller and Lazareva (2013)
[9]RAPPORT d'etude (2013)
[10]Zhang and Saebfar (2010)
[11]Aschberger et al. (2011)
[12]RAPPORT d'etude (2013)
[13]Future Markets (2012)
[14]Blaser et al. (2008)
[15]Windler et al. (2013)
[16]Sahasrabudhe (2010)
[17]Personal communication with industry people at RAS Materials in Germany (2014)
[18]Ray et al. (2009)
[19]Healy et al. (2008)

Table C.1: Raw data of production volume of nano-TiO_2, nano-ZnO, nano-Ag and CNT in 2012 in Europe with Degree of Belief (DoB) for modelling the base year 2012's production distribution

ENMs	**80% Degree of Belief**	**20% Degree of Belief**
Nano-TiO2	246[1]	4'037[2]
	55-3'000[3]	49'373[4]
	8'674-42'256[5]	1'285[6]
	13'398[7]	
	13'360-14'080[8]	
	90'216[9]	
Nano-ZnO	2'151[7]	6[6]
	5.5-28'000[3]	136[10]
	5'040-5'440[8]	2'570 [11]
	1'815[12]	
Nano Ag	15[13]	129[10]
	0.6-55[3]	11-23[14]
	1.2-41[15]	13-26[16]
	92[7]	
	3.1-22[5]	
	1[17]	
	58-72[8]	
CNT	848[13]	129[1118]
	180-550[3]	353[19]
	31[7]	
	61-1'224[5]	
	467-512[8]	

Table C.2: Summary of nanotechnology development projection and patents analysis used for extrapolation of ENM production development. Data marked in green are the data without reach to 2012; data marked in orange are the data with coverage of 2012. The column for the year 2005 makes the connection between "green" data and "orange" data. The column for 2012 is the reference year on which basis the other years' ratios were calculated.

	Sources\Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
General nanotechnology	**Patents analysis**																	
	Scheu et al. 2006						0.261	0.317	0.328	0.348	0.352	0.452	0.488	0.539	0.724	0.980	1	
	Dorsey											0.240	0.301	0.385	0.526	0.769	1	1.137
	Parrish 2010												0.457	0.549	0.665	0.814	1	1.243
	Daim 2007			0.000	0.000	0.011	0.027	0.016	0.022	0.032	0.033	0.054	0.069	0.106	0.132	0.174	0.248	0.316
	Chen 2008 USPO	0.053	0.088	0.077	0.115	0.164	0.166	0.173	0.217	0.277	0.322	0.402	0.497	0.571	0.709	0.788	1	1.260
	Chen 2008 EPO	0.063	0.066	0.129	0.096	0.077	0.115	0.184	0.201	0.195	0.255	0.308	0.343	0.387	0.646	0.846	1	1.313
	Chen 2008 JPO	0.056	0.042	0.091	0.203	0.322	0.315	0.490	0.455	0.462	0.357	0.378	0.545	0.608	0.587	0.811	1	0.881
	Berger 2006												0.254	0.349	0.480	0.673	1	1.398
	Dang et al. 2010				0.060	0.087	0.088	0.101	0.108	0.129	0.149	0.190	0.230	0.304	0.445	0.813	1	1.642
	Market projection																	
	Future Markets																	
	BCC Research													0.452			0.525	0.525
	Lux Research															0.033	0.033	0.056
	Roco et al.2011											0.083	0.093	0.116	0.144	0.178	0.248	0.274
	EC report Optimistic												0.000	0.052	0.082	0.148	0.207	0.281
	EC Report Pessimistic												0.000	0.004	0.066	0.109	0.120	0.163
CNT specific	**Patents analysis**																	
	Nanowerk 2011												0.120	0.235	0.375	0.619	1	1.716
	Dorsey CNT											0.070	0.141	0.230	0.722	0.767	1	1.689
	Market projection																	
	BCC Research											0.020	0.032	0.048	0.072	0.104	0.148	0.204
	Piccinno et al. 2012														0.003	0.050	0.083	0.228
	Future Markets																	
	Nanowerk 2011																	


General nanotechnology
CNT specific
Year
2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020
Patents analysis
Scheu et al. 2006
Dorsey
Parrish 2010 1.490 1.727 2.164 2.645 3.341
Daim 2007 0.410 0.509 0.640 0.770 0.890 1 1.094 1.193 1.246 1.298 1.335 1.366 1.382 1.403
Chen 2008 USPO 1.199 1.564
Chen 2008 EPO 1.651 1.865
Chen 2008 JPO
Berger 2006 1.756 1.851
Dang et al. 2010 2.183 2.538 2.725 3.253
Market projection
Future Markets 0.968 1 1.043 1.094 1.151 1.226
BCC Research 0.672 0.711 0.583 0.649 0.984 1 1.235 1.323 1.529 1.865 2.468
Lux Research 0.089 0.133 0.233 0.356 0.656 1 1.400 1.800
Roco et al.2011 0.340 0.422 0.517 0.650 0.806 1 1.240 1.539 2.069 2.368 2.937 3.644 4.520 6.207
EC report Optimistic 0.354 0.428 0.531 0.648 0.802 1 1.220 1.483 1.813 2.227
EC Report Pessimistic 0.205 0.279 0.333 0.438 0.643 1 1.457 2.217 3.027 3.752
Patents analysis
Nanowerk 2011 2.450 2.642
Dorsey CNT
Market projection
BCC Research 0.316 0.372 0.412 0.668 0.800 1 1.224 1.492 1.796 2.140
Piccinno et al. 2012
Future Markets 0.215 0.387 0.770 0.845 0.876 1 1.123
Nanowerk 2011 0.884 1 1.121 1.394 1.606 2.045
Scheu et al. 2006 0.787 1 1.302 1.728 2.319 3.207

Colloidal silver has been used for medical applications since 120 years (Nowack et al., 2011). This means nano silver has been long used before the term "nano-Ag" was invented. To take all the man-made nano-Ag actually applied in history into account, besides the time from 1990 to 2020, for nano-Ag we also modelled another period from 1900 to 2020, which represents a more realistic history of nano-Ag application. In this case, the production distribution of nano-Ag in 2012 is still used as the base. The scaling factor for each individual year is made under the assumption that there is a linear increase of the nano-Ag share compared to total Ag produced worldwide from 1900 to 2020 (U.S. Geological Survey, 2014). By combining this information with the data of the development of total Ag production the scaling factor for each individual year is obtained.

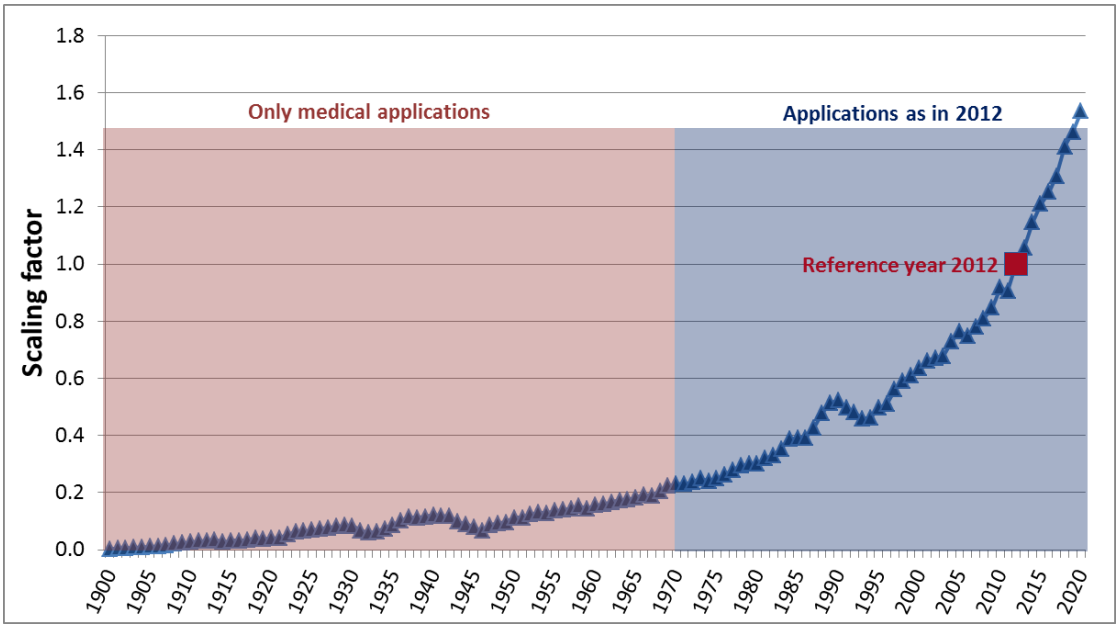
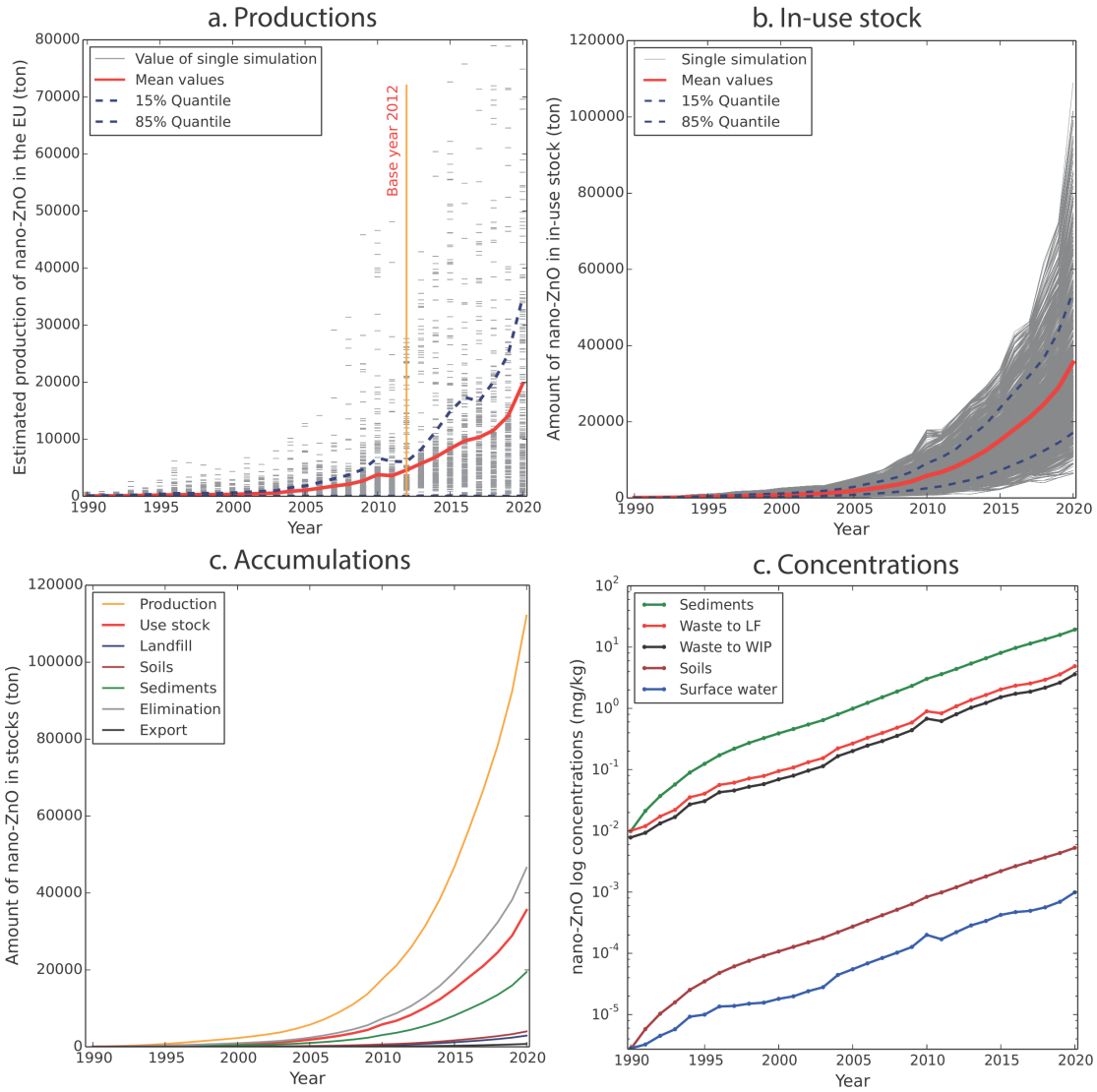
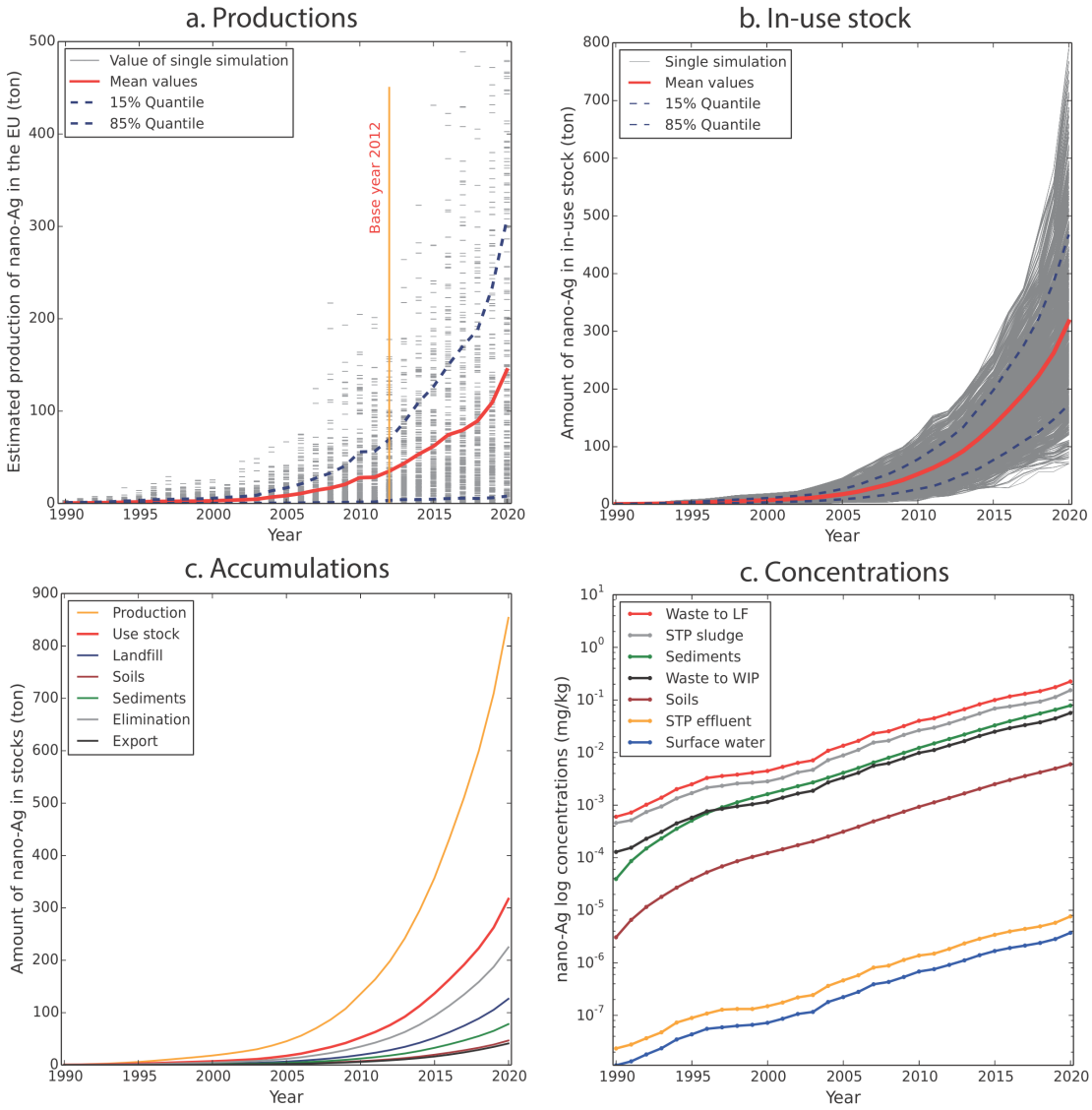
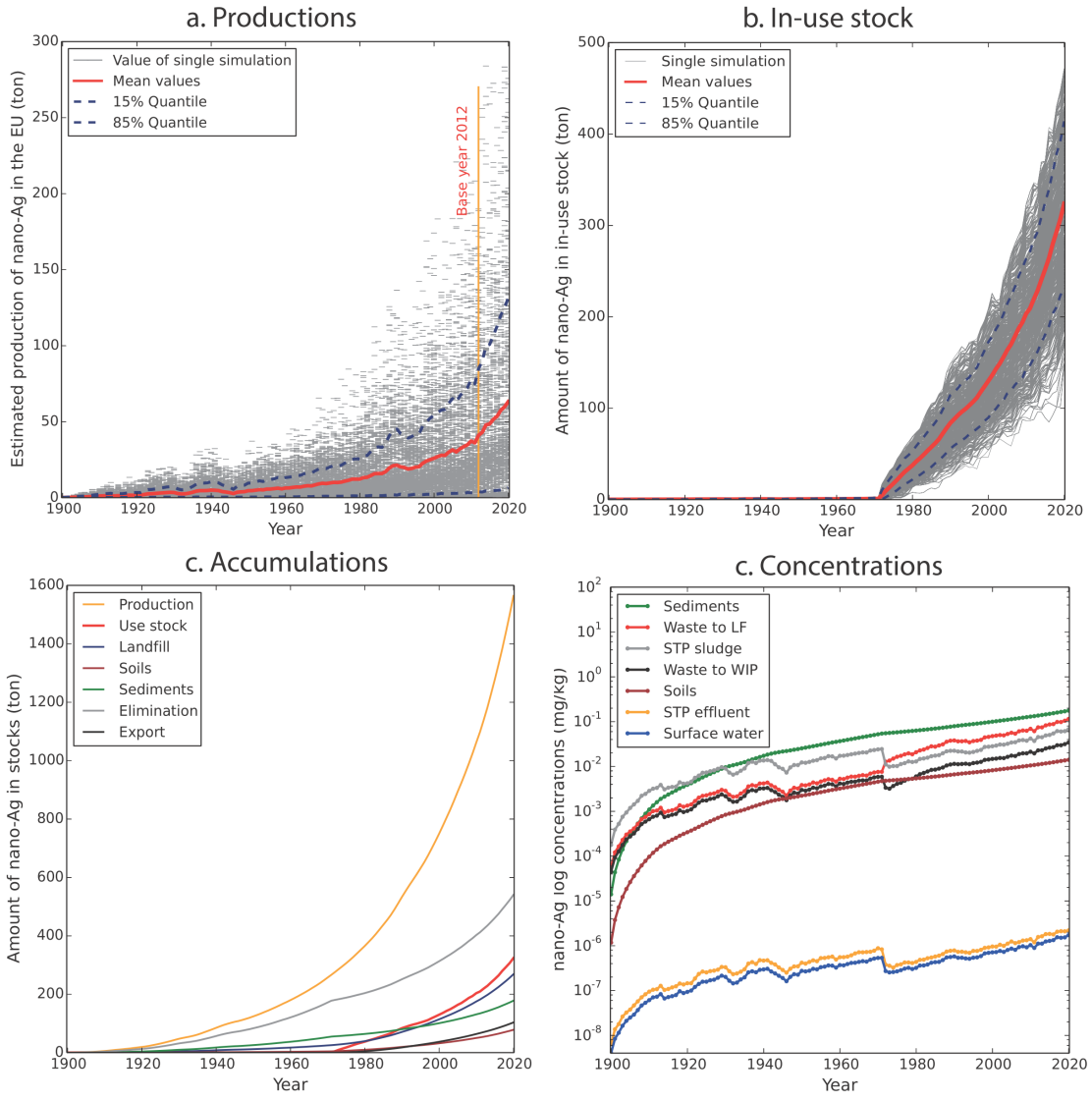


Figure C.1: Estimated scaling factor for production development of nano-Ag from 1900 to 2020. The year 2012 is taken as a reference year. The curve is obtained based on the information of development of total Ag production and the assumed linear increase of the share of nano-Ag compared to total Ag from 1900 to 2020. The use of nano-Ag from 1900 to 1970 is assumed to be only for medical applications; from 1970 to 2020 applications of nano-Ag is assumed to be the same as in the year of 2012.


a. Productions
Estimated production of nano-ZnO in the EU (ton)
Value of single simulation
Mean values
15% Quantile
85% Quantile
Base year 2012
Year
b. In-use stock
Amount of nano-ZnO in in-use stock (ton)
Single simulation
Mean values
15% Quantile
85% Quantile
Year
c. Accumulations
Amount of nano-ZnO in stocks (ton)
Production
Use stock
Landfill
Soils
Sediments
Elimination
Export
Year
c. Concentrations
nano-ZnO log concentrations (mg/kg)
Sediments
Waste to LF
Waste to WIP
Soils
Surface water
Year


a. Productions
Value of single simulation
Mean values
15% Quantile
85% Quantile
Base year 2012
Estimated production of nano-Ag in the EU (ton)
Year
b. In-use stock
Single simulation
Mean values
15% Quantile
85% Quantile
Amount of nano-Ag in in-use stock (ton)
Year
c. Accumulations
Production
Use stock
Landfill
Soils
Sediments
Elimination
Export
Amount of nano-Ag in stocks (ton)
Year
c. Concentrations
Waste to LF
STP sludge
Sediments
Waste to WIP
Soils
STP effluent
Surface water
nano-Ag log concentrations (mg/kg)
Year


a. Productions
Value of single simulation
Mean values
15% Quantile
85% Quantile
Base year 2012
Estimated production of nano-Ag in the EU (ton)
Year
b. In-use stock
Single simulation
Mean values
15% Quantile
85% Quantile
Amount of nano-Ag in in-use stock (ton)
Year
c. Accumulations
Production
Use stock
Landfill
Soils
Sediments
Elimination
Export
Amount of nano-Ag in stocks (ton)
Year
c. Concentrations
Sediments
Waste to LF
STP sludge
Waste to WIP
Soils
STP effluent
Surface water
nano-Ag log concentrations (mg/kg)
Year

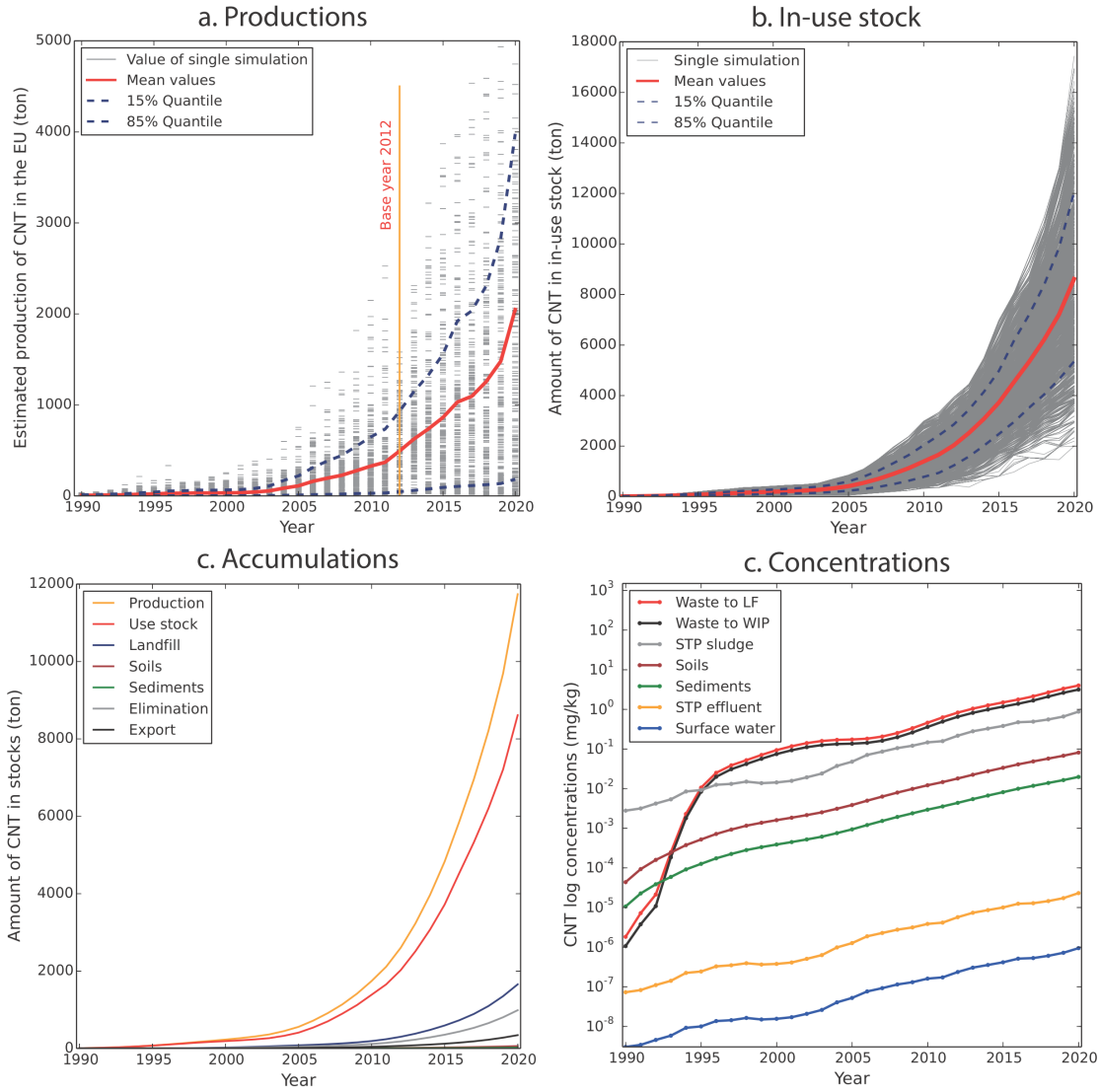


Figure C.2: **a.** modelled production development of nano-ZnO, nano-Ag (from 1900 to 2020 and from 1990 to 2020), CNT in the EU from 1990 to 2020. Short grey lines indicate the single modelled values. The red curve is the average trend out of the whole simulated values. Dashed blue lines indicate the quantile 15% and 85% range showing the range of the prob-ability density distribution of the production. **b.** the evolution of nano-TiO_2 amount in the in-use stock The grey lines are development trend of single simulations out of 100 thousands of simulations. The average and quantile 15% and 85% are also shown. The whole cluster area consisting of grey curves builds up the range of the probability distribution of the overall trend. The vertical width of the grey area indicates the degree of uncertainty. **c.** the evolution of nano-TiO_2 in the in-use stock and in landfills, sludge treated soils and sediments as well as the total accumulative production in the EU from 1990 to 2020. Average values are taken here. **d.** the concentrations evolution in the important technical and environmental compartments in logarithmic scale. "Soils" here indicate the STP sludge treated soils; "LF"=Landfill, "WIP"=waste incineration plant.

C.2. Release parameters

The release schedules were determined based on empirical data if relevant experimental data were available, or on the basis of expert opinions, if no relevant data were available. To quantify and schedule the time-dependent release during use, we searched for all the available studies regarding ENM release over time. A handful of studies for some important nanomaterials and applications are available that make a detailed modelling possible. Among the four ENM studied, most studies are available for nano-TiO_2. These studies are mainly about release from textile and paints. Kaegi et al. (2010) conducted a one-year long experiment on a model facades to investigate the release of nano-Ag (to certain extent also TiO_2). The cumulative TiO_2 release was about 1%. A clear decrease over the first half year was observed and for the rest almost no further release was observed. Al-Kattan et al. (2013) studied the release of nano-TiO_2 from paints by weathering. Their results show that after 120 cycles of weathering less than 1% of nano-TiO_2 was released to waster. A study conducted by Windler et al. (2012) investigated the nano-TiO_2 release from textiles during washing. After ten cycles of washing experiment, functional textiles released some TiO_2 particles, normally less than 1% of the initial content. In another study by Olabarrieta et al. (2012), TiO_2 nanoparticles release from glasses under water flow was observed over a four-week experiment duration. No information of percentage of nano-TiO_2 loss and the distribution of TiO_2 release over time was given.

Several studies about nano-Ag release from product such as textiles are available. von Goetz et al. (2013) and Lorenz et al. (2012) investigated the nano-Ag migration into artificial sweat under physical stress and nano-Ag release from commercially available functional textiles respectively. They showed that up to 20% of nano-Ag can be released from textiles, but no information about the temporal development is available. So the results cannot be used for the purpose of time dependent ENM release modelling. Another unpublished work by Limpiteeprakan et al. (2016) looked at release of Ag from three commercial textiles, one cotton based, one PET based and one TC based. After ten washes, 51%, 65% and 48% of nano-Ag was released into washing solution (lab water without detergent). After 20 times wash, the numbers were 55%, 72%, and 48%, respectively. This indicates that the release distribution over time follows a dramatically declining trend. The major release occurred during the first washing cycles.

Priority (share of the total nano-TiO_2 application)[a]	nano-TiO_2 (product categories)	Use release	Use release duration (years)	Use release schedule					Distribution after use release[b]				EoL release	Lifetime distribution (normal) Note: σ is the standard deviation	Distribution after EoL release			
		X		Y1	Y2	Y3	Y4	...	Wastewater	Air	Surface water	Soil	1-X		Landfill	WIP	Recycling	Export
59.4%	Cosmetics	0.95[b]	2[c]	0.9[c]	0.1[c]				0.9		0.1		0.05[b]	Y1=0.90, Y2=0.10[c]	0.35[d]	0.25[d]	0.40[e]	
8.9%	Paints	0.01[f]	7[g]	0.9[f]	0.1*(1/6)[c][f]				0.5	0.25		0.25	0.99[f]	mean=80; 3σ=20[c][h]	0.3[i]		0.7[i]	
6.9%	Electronics & A	0.30[c]	8[j]	0.1*(1/8)[c]					1				0.70[c]	mean=8; 3σ=8[j][c]	0.1[d]	0.05[d]	0.65[k]	0.2[l]
6.2%	Cleaning agent	0.95[b]	1[c]	1.0[c]					1				0.05[b]	Y1=1.0[c]	0.35[d]	0.25[d]	0.40[e]	
5.8%	Filter	0.30[a]	8[g]	1/8[c]					0.8	0.2			0.70[a]	mean=8; 3σ=8[c][g]	0.1[d]	0.05[d]	0.65[k]	0.2[l]
3.6%	Plastics	0.03[m]	8[c]	1/8[c]					1				0.97[m]	mean=8; 3σ=5[c]	0.35[d]	0.25[d]	0.40[e]	
3.7%	Coating	0.35[n]	10[c]	0.9[n]	0.1*(1/9)[c]				0.8	0.1		0.1	0.65[n]	mean=10; 3σ=5[c]	0.35[d]	0.25[d]	0.40[e]	
1.7%	Glass & Ceramics	0.35[n]	10[c]	0.9[n]	0.1*(1/9)[c]				1				0.65[n]	mean=10; 3σ=5[c]	0.20[k]	0.10[k]	0.7[p]	
1.5%	Sport goods	0.04[a]	7[c]	1/7[c]					0.7	0.3			0.96[a]	mean=7; 3σ=3[c]	0.35[d]	0.25[d]	0.40[e]	
0.7%	WWTP	0.98[b]	1[c]	1.0[c]					1				0.02[b]	Y1=1.0[c]	0.6[d]	0.4[d]		
0.4%	Batteries	0[a]											1.00[a]	mean=4; 3σ=2	0.45[k]	0.30[k]	0.25[l]	
0.4%	Food	0.90[a]	1[c]	1.0[c]					1				0.10[a]	Y1=1.0[c]	0.6[d]	0.4[d]		
0.3%	Textiles	0.03[b]	3[o]	0.5[m]	0.3[m]	0.2[m]			0.8	0.2			0.97[b]	mean=3; 3σ=2[o]	0.31[p]	0.07[p]	0.28[p]	0.34[p]
0.2%	Light Bulbs	0[a]											1.00[a]	mean=4; 3σ=2[q]	0.35[d]	0.25[d]	0.40[e]	
0.2%	Spray	0.95[a]	1[c]	1.0[c]					0.9	0.1			0.05[a]	Y1=1.0[c]	0.35[d]	0.25[d]	0.40[e]	
0.1%	Metals	0.05[a]	20[c]	1/20[c]					1				0.95[a]	mean=20; 3σ=5[c]	0.03[d]	0.02[d]	0.95[p]	
0.1%	Cement	0.01[a]	80[h]	0.9[c]	1/79[c][h]				1				0.99[a]	mean=80; 3σ=20[h]	0.3[i]		0.7[i]	
<0.1%	Ink	0[c]											1.00[c]	mean=5; 3σ=4[c]	0.07[d]	0.03[d]	0.7[r]	0.2[r]
<0.1%	Paper	0[c]											1.00[c]	mean=5; 3σ=4[c]	0.07[d]	0.03[d]	0.7[r]	0.2[r]

Priority (share of the total nano-ZnO application)[a]	nano-ZnO (product categories)	Use release	Use release duration (years)	Use release schedule					Distribution after use release[b]				EoL release	Lifetime distribution (normal) Note: σ is the standard deviation	Distribution after EoL release			
		X		Y1	Y2	Y3	Y4	...	Wastewater	Air	Surface water	Soil	1-X		Landfill	WIP	Recycling	Export
82.6%	Cosmetics	0.95[b]	2[c]	0.9[c]	0.1[c]				0.9		0.1		0.05[b]	Y1=0.90, Y2=0.10[c]	0.35[d]	0.25[d]	0.40[e]	
14.3%	Paints	0.35[r]	7[g]	0.9[f]	0.1*(1/6)[c][f]				0.5	0.25		0.25	0.65[r]	mean=80; 3σ=20[c][h]	0.3[i]		0.7[i]	
2.0%	Plastics	0.80[c]	8[c]	1/8[c]					1				0.20[c]	mean=8; 3σ=5[c]	0.35[d]	0.25[d]	0.40[e]	
0.7%	Glass	0.35[r]	10[c]	0.9[c]	0.1*(1/9)[c]				1				0.65[r]	mean=10; 3σ=5[c]	0.20[d]	0.10[d]	0.7[s]	
0.2%	Electronics &A	0.30[c]	8[j]	0.1*(1/8)[c]					1				0.70[c]	mean=8; 3σ=8[j][c]	0.1[d]	0.05[d]	0.65[k]	0.2[l]
0.1%	Filter	0.30[a]	8[g]	1/8[c]					0.8	0.2			0.70[a]	mean=8; 3σ=8[c][g]	0.1[d]	0.05[d]	0.65[k]	0.2[l]
0.1%	Cleaning agent	0.95[b]	1[c]	1.0[c]					1				0.05[b]	Y1=1.0[c]	0.35[d]	0.25[d]	0.40[e]	
< 0.1%	Foods	0.90[a]	1[c]	1.0[c]					1				0.10[a]	Y1=1.0[c]	0.6[d]	0.4[d]		
< 0.1%	Textiles	0.60[t]	3[o]	0.7[t]	0.2[t]	0.1[t]			0.80	0.20			0.40[t]	mean=3; 3σ=2[o]	0.31[p]	0.07[p]	0.28[p]	0.34[p]
< 0.1%	Metals	0.05[a]	20[c]	1/20[c]					1				0.95[a]	mean=20; 3σ=5[c]	0.03[d]	0.02[d]	0.95[p]	
< 0.1%	Woods	0.30[c]	20[c]	1/20[c]					1				0.70[c]	mean=20; 3σ=10[c]		1[c]		
< 0.1%	Paper	0[c]											1.00[c]	mean=5; 3σ=4[c]	0.07[d]	0.03[d]	0.7[r]	0.2[r]

Priority (share of the total CNT application)[a]	CNT (product categories)	Use release	Use release duration (years)	Use release schedule					Distribution after use release[b]				EoL release	Lifetime distribution (normal) Note: σ is the standard deviation	Distribution after EoL release			
		X		Y1	Y2	Y3	Y4	...	Wastewater	Air	Surface water	Soil	1-X		Landfill	WIP	Recycling	Export
84.1%	Composites	0.01[c]	7[c]	1/7[c]						0.2		0.8	0.99[c]	mean=7; 3σ=3[c]	0.35[d]	0.25[d]	0.40[e]	
9.1%	Energy	0[c]											1.00[c]	mean=15; 3σ=5[u]	0.1[d]	0.05[d]	0.65[k]	0.2[l]
3.1%	Electronics &A	0[c]											1.00[c]	mean=8; 3σ=8[j][c]	0.1[d]	0.05[d]	0.65[k]	0.2[l]
1.4%	Paints	0.01[f]	7[g]	0.9[f]	0.1*(1/6)[c][f]				0.5	0.25		0.25	0.99[f]	mean=80; 3σ=20[h]	0.3[i]		0.7[i]	
1.3%	Automotive	0[c]											1.00[c]	mean=12; 3σ=5[v]	0.3[a]	0.1[a]	0.4[a]	0.2[a]
0.6%	Aerospace	0[c]											1.00[c]	mean=20; 3σ=5[c]	0.3[c]	0.1[c]	0.6[c]	
0.4%	Sensor	0[c]											1.00[c]	mean=8; 3σ=8 [c]	0.1[d]	0.05[d]	0.65[k]	0.2[l]
< 0.1%	Textiles	0.03[b]	3[o]	0.5[m]	0.3[m]	0.2[m]			0.8	0.2			0.97[b]	mean=3; 3σ=2[o]	0.31[p]	0.07[p]	0.28[p]	0.34[p]

Note: Yn = year n, e.g. Y1= year 1; Electronics & A.= "Electronics and Appliances"
(a) Sun et al. (2014), (b) revised based on Sun et al. (2014), (c) expert judgment, (d) Bakas et al. (2011), (e) EEA Website (2013), (f) Al-Kattan et al. (2013), (g) ATD Home inspection (2014), (h) Hischier et al. (2015), (i) EEA (2009), (j) Streicher-Porte (2014), (k) Kiddee et al. (2013), (l) EEA (2012), (m) Windler et al. (2012), (n) Olabarrieta et al. (2012), (o) Eastonstewartsville drycleaner Webpage (2014), (p) Friend of the Earth Europe (2013), (q) The Telegraph (2009), (r) Kaegi et al. (2010), (s) Glass International (2014), (t) Limpiteeprakan et al. (2016), (u) Energy Informative (2014), (v) Kraftfahrt Bundesamt (2003)

Table C.3: Summary of use phase and EoL release for ENM (nano-TiO_2, nano-ZnO and CNT). Column "Priority" is based on the share of ENM applied in products categories. Values of "X" in column "Use release" indicate the fraction of ENM contained in a product released during the use phase; values of "1-X" in column "EoL release" indicate the fraction of ENM released during the product's end of life (EoL). "Use release duration" means the estimated number of years in which release takes place; "Use release schedule" is the schedule that each year after a product enters the system how much ENM is released; "Distribution after use release" is the allocation factor to different environmental compartments after ENM is released during use; Life time of products categories are assumed as being normally distributed. Average life time and deviations are either based on literature if available or estimated based on expert judgement. Similar to "Distribution after EoL release", "Distribution after EoL release" describes the allocations of ENM flows when they come to the end of their life.

Table C.4: Summary of volumes of different technical and environmental compartments used for the EU

Compartments	Formula	Volumes	Unit	Comments
Air	4'326'337*1*10^9	4.33E+15	m^3	4'326'337 km^2,is the area of EU27[20], 10 days was used for the residence time in air for ultrafine particles[21], 1 km was taken for the depth of air will be affected by ENM[22], 10^9 is the transformation from km^3 to m^3
Natural and urban soil	4'326'337*0.97*10^6*(0.2*0.47+0.05*0.53)*1'500	7.59E+14	kg	0.97 is the proportion of terrestrial land,in EU[20], 10^6 is the transformation factor from km^2,to m^2, 0.2 is the depth considered for,agricultural soil suggested[22], 0.47 is the share of agricultural land area,in EU[23], 0.05 m depth of natural and urban soil[22], 0.53 is the share of natural and urban land,in EU[23], 1'500 kg/m^3 is the density of dry soil[22]
Biosolid treated soil	(9'000'000*0.55/20),*10^4*0.2*1'500	7.43E+11	kg	9'000'000 tons is the volume of sewage,sludge EU yearly produced[24], 0.55 is the share of sewage sludge going to,agricultural soil[25], 20 tons/ha is the average sludge,application rate in EU[26], 10^4 is the transformation factor from ha^2 to m^2
Surface water	4'326'337*0.03*10^6*3*1'000	3.89E+14	litre	0.03 is the share of water area in EU[20], 3 m is the depth of water compartment,considered[22], 1'000 is the transformation factor from m3 to litre
Sediments	4'326'337*0.03*10^6*0.03*260	1.01E+12	kg	0.03 m is the depth of sediments considered,to be affect by ENM[22], The another 0.03 is the share of water area,in EU[20], 260 kg/m^3,is the density of sediments soil[27]
STP Effluent	0.8*200*365*509'000'000	2.97E+13	litre	0.8 is the average proportion of EU,families connected to central sewage facility[22], 200 l/head is the average daily water,consumption of EU citizens [22], 509'000'000 is the number of EU population[20]
STP Sludge		9.00E+09	kg	9'000'000'000 kg is the volume of sewage sludge EU yearly produced[24]
Solid Waste landfilled		7.31E+10	kg	73.1 million tonnes of municipal waste is landfilled in the EU in 2013[28]
Solid Waste incinerated		6.16E+10	kg	61.6 million tonnes of municipal waste is incinerated in the EU in 2013[28]

[20]Wikipedia (2012)
[21]Anastasio and Martin (2001)
[22]ECB (2003)
[23]The European Commission – Press release database (2013)
[24]EC (2009)
[25]Blaser et al. (2008)
[26]Eamens et al. (2006)
[27]Gottschalk et al. (2009)
[28]Eurostat (2015)

Figure C.3: Predicted (Accumulated) concentrations of nano-TiO^2, nano-ZnO, nano-Ag and CNT in waste streams and environmental compartments in the EU in 2020. Mean, mode, median, quantile 0.15 and quantile 0.85 are shown. Values are rounded off to three significant digits. Results for nano-Ag are presented for both the time scopes of the 1900-2020 and 1990-2020 scenarios.

	EU (2020)					
	Mean	**Mode**	Median	$Q_{0.15}$	$Q_{0.85}$	
Nano-TiO_2						
STP Effluent	111	22	26.7	3.56	189	µg/L
STP sludge	4.11	0.966	1.594	0.222	6.99	g/kg
Solid waste to Landfill	37.0	24.6	29.7	16.0	56.6	mg/kg
Solid waste to WIP	29.7	19.2	23.4	12.1	45	mg/kg
WIP bottom ash	1.06	0.373	0.571	0.234	1.73	g/kg
WIP fly ash	1.45	0.545	0.762	0.308	2.27	g/kg
Surface water	5.55	1.34	2.06	0.292	9.59	µg/L
Sediment	117	80.4	104	59.5	175	mg/kg
Natural and urban soil	6.27	4.03	5.38	2.90	9.62	µg/kg
Sludge treated soil	0.166	0.118	0.151	0.083	0.248	g/kg
Air	3.72	0.648	1.20	0.141	6.35	ng/m^3
Nano-ZnO						
STP Effluent	0.000	0.000	0.000	0.000	0.000	µg/L
STP sludge	0.000	0.000	0.000	0.000	0.000	µg/kg
Solid waste to Landfill	4.86	2.51	3.02	1.26	7.31	mg/kg
Solid waste to WIP	3.60	1.43	2.13	0.811	5.73	mg/kg
WIP bottom ash	18.1	7.37	10.0	3.41	28.9	mg/kg
WIP fly ash	35.2	14.5	17.6	5.12	59.3	mg/kg
Surface water	0.987	0.280	0.444	0.047	1.63	µg/L
Sediment	19.3	14.0	16.9	10.0	29.0	mg/kg
Natural and urban soil	5.27	3.50	4.37	2.10	8.39	µg/kg
Sludge treated soil	5.27	3.50	4.37	2.10	8.39	µg/kg
Air	2.50	0.817	0.979	0.115	4.22	ng/m^3
Nano-Ag (1990-2020)						
STP Effluent	2.46	0.629	0.918	0.160	4.43	ng/L
STP sludge	148	31.8	55.6	9.82	260	µg/kg
Solid waste to Landfill	224	96.9	121.4	43.0	384	µg/kg
Solid waste to WIP	56.2	28.7	36.8	16.9	95.2	µg/kg
WIP bottom ash	498	297	405	223	765	µg/kg
WIP fly ash	0.976	0.485	0.742	0.308	1.64	mg/kg
Surface water	3.66	1.15	1.97	0.450	7.21	ng/L
Sediment	77.0	65.0	70.6	44.4	111	µg/kg
Natural and urban soil	0.056	0.041	0.051	0.032	0.081	µg/kg
Sludge treated soil	5.91	1.93	4.72	1.13	10.9	µg/kg
Air	0.029	0.010	0.017	0.004	0.054	ng/m^3
Nano-Ag (1900-2020)						
STP Effluent	4.86	1.23	2.12	0.482	8.49	ng/L
STP sludge	67.5	21.5	34.1	7.26	133	µg/kg
Solid waste to Landfill	114	53.7	75.2	34.2	196	µg/kg
Solid waste to WIP	34.1	19.1	26.6	14.9	56.0	µg/kg
WIP bottom ash	370	289	333	195	552	µg/kg
WIP fly ash	0.740	0.397	0.606	0.261	1.23	mg/kg
Surface water	1.73	0.731	1.01	0.368	3.42	ng/L
Sediment	179	175	175	137	220	µg/kg
Natural and urban soil	0.090	0.081	0.086	0.061	0.118	µg/kg
Sludge treated soil	14.1	4.49	12.6	3.20	25.6	µg/kg
Air	0.013	0.006	0.009	0.003	0.025	ng/m^3
CNT						
STP Effluent	23.0	5.47	13.7	1.99	46.3	ng/L
STP sludge	0.872	0.189	0.542	0.078	1.72	mg/kg
Solid waste to Landfill	3.99	3.11	3.68	2.19	5.77	mg/kg
Solid waste to WIP	3.14	2.62	2.89	1.68	4.61	mg/kg
WIP bottom ash	1.39	0.524	1.04	0.316	2.49	mg/kg
WIP fly ash	2.85	0.888	1.82	0.486	5.31	mg/kg
Surface water	0.939	0.221	0.585	0.088	1.81	ng/L
Sediment	19.7	16.0	18.6	12.5	26.7	µg/kg
Natural and urban soil	46.5	42.8	44.5	30.1	62.9	ng/kg
Sludge treated soil	34.5	26.8	32.5	21.8	46.8	µg/kg
Air	0.038	0.008	0.023	0.003	0.075	ng/m^3

References of the Appendix Part

Al-Kattan, A., Wichser, A., Vonbank, R., Brunner, S., Ulrich, A., Zuin, S., and B., N. (2013). Release of TiO^2 from paints containing pigment-TiO^2 or nano-TiO^2 by weathering. Environmental Science Processes & Impacts, 15(12):2186–2193.

Anastasio, C. and Martin, S. T. (2001). Atmospheric nanoparticles, volume 44 of Reviews in Mineralogy & Geochemistry, pages 293–349.

Aschberger, K., Micheletti, C., Sokull-Kluttgen, B., and Christensen, F. M. (2011). Analysis of currently available data for characterising the risk of engineered nanomaterials to the environment and human health - lessons learned from four case studies. Environment International, 37(6):1143–1156.

ATD Home inspection (2014). Average life span of homes, appliances, and mechanicals. *http://www.atdhomeinspection.com/advice/average-product-life/*, Accessed: 2015-06-06.

Bakas, I., Sieck, M., Hermann, T., Andersen, F. M., and Larsen, H. (2011). Projections of municipal waste management and greenhouse gases. Technical report, European Environment Agency.

bcc Research (2012). Nanotechnology: A realistic market assessment. *http://www.bccresearch.com/market-research/nanotechnology/nanotechnology-market-applications-products-nan031e.html*, Accessed: 2014-11-19.

Berger, M. (2006). The patent land grab in nanotechnology continues unabated, creating problems down the road. *Availablefrom:http://www.nanowerk.com/spotlight/spotid=386.php*, Accessed: 2014-11-19.

Blaser, S. A., Scheringer, M., MacLeod, M., and Hungerbuhler, K. (2008). Estimation of cumulative aquatic exposure and risk due to silver: Contribution of nano-functionalized plastics and textiles. Science of the Total Environment, 390(2-3):396–409.

Chen, H., Roco, M. C., Li, X., and Lin, Y. (2008). Trends in nanotechnology patents. Nature Nanotechnology, 3(3):123–125.

Daim, T., Monalisa, M., Dash, P., and Brown, N. (2007). Time lag assessment between research funding and output in emerging technologies. Foresight, 9(4):33–44.

Dang, Y., Zhang, Y., Fan, L., Chen, H., and Roco, M. C. (2010). Trends in worldwide nanotechnology patent applications: 1991 to 2008. Journal of Nanoparticle Research, 12(3):687–706.

DORSEY (2005). Nanotechnology patents-trends in the united states patent office. *http://www.dorsey.com/Nanotechnology-Patents--Trends-in-the-United-States-Patent-Office-05-09-2005/*, Accessed: 2014-11-19.

Eamens, G. J., Waldron, A. M., and Nicholls, P. J. (2006). Survival of pathogenic and indicator bacteria in biosolids applied to agricultural land. Australian Journal of Soil Research, 44(7):647–59.

Eastonstewartsville drycleaner Webpage (2014). The average life expectancy of clothing. *https://eastonstewartsvilledrycleaner36.wordpress.com/2010/11/30/the-average-life-expectancy-of-clothing/*, Accessed: 2014-11-19.

EC (2009). European commission sewage sludge. *http://ec.europa.eu/environment/waste/sludge/index.htm*, Accessed: 2014-11-19.

ECB (2003). Technical guidance document on risk assessment. Technical report, Dublin: European Chemicals Bureau; Institute for Health and Consumer Protection.

EEA (2009). EU as a recycling society present recycling levels of municipal waste and construction & demolition waste in the EU. Technical report, European Topic Centre on Sustainable Consumption and Production.

EEA (2012). Movements of waste across the EU's internal and external borders. Technical Report ISSN 1725-9177, European Environment Agency.

EEA Website (2013). Municipal waste recycling rates in 32 european countries, 2001 and 2010. *https://www.eea.europa.eu/data-and-maps/figures/municipal-waste-recycling-rates-in*, Accessed: 2014-11-19.

Energy Informative (2014). The real lifespan of solar panels. *http://energyinformative.org/lifespan-solar-panels/*, Accessed: 2014-11-19.

EPA, US Environmental Protection Agency (2010). Nanomaterial case studies: Nanoscale titanium dioxide in water treatment and in topical sunscreen. Technical report. *https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=230972*, Accessed: 2017-12-10.

European Commission (2006). The economic development of nanotechnology - an indicators based analysis. Technical report.

Eurostat (2015). Municipal waste statistics. *http://ec.europa.eu/eurostat/statistics-explained/index.php/Municipal_waste_statistics#Municipal_waste_treated_in_Europe*, Accessed: 2015-04-16.

Friend of the Earth Europe (2013). Less is more, resource efficiency through waste collection, recycling and reuse of aluminium, cotton and lithium in europe.

Future Markets (2012). Nanomaterials in plastics and advanced polymers. Technical Report 52.

Glass International (2014). Eu glass recycling rate passes 70% mark. *http://www.glass-international.com/news/view/eu-glass-recycling-rate-passes-70-mark*, Accessed: 2014-11-19.

Gottschalk, F., Sonderer, T., Scholz, R. W., and Nowack, B. (2009). Modeled environmental concentrations of engineered nanomaterials (TiO2, ZnO, Ag, CNT, fullerenes) for different regions. Environmental Science and Technology, 43:9216–9222.

Healy, M. L., Dahlben, L. J., and Isaacs, J. A. (2008). Environmental assessment of single-walled carbon nanotube processes. Journal of Industrial Ecology, 12(3):376–393.

Hendren, C. O., Mesnard, X., Dröge, J., and Wiesner, M. R. (2011). Estimating production data for five engineered nanomaterials as a basis for exposure assessment. Environmental Science and Technology, 45(7):2562–2569.

Hischier, R., Nowack, B., Gottschalk, F., Hincapie, I., Steinfeldt, M., and Som, C. (2015). Life cycle assessment of façade coating systems containing manufactured nanomaterials. Journal of Nanoparticle Research, 17(2):1–13.

Kaegi, R., Sinnet, B., Zuleeg, S., Hagendorfer, H., Mueller, E., Vonbank, R., Boller, M., and Burkhardt, M. (2010). Release of silver nanoparticles from outdoor facades. Environmental Pollution, 158(9):2900–2905.

Keller, A. A. and Lazareva, A. (2013). Predicted releases of engineered nanomaterials: From global to regional to local. Environmental Science & Technology Letters, 1(1):65–70.

Kiddee, P., Naidu, R., and Wong, M. H. (2013). Electronic waste management approaches: An overview. Waste Management, 33(5):1237–1250.

Kraftfahrt Bundesamt (2003). Pressemitteilung Nr. 30/2003 - Alter Fahrzeugbestand.

Limpiteeprakan, P., Babel, S., Lohwacharin, J., and S., T. (2016). Release of silver nanoparticles by sequential washing and bactericidal effects of silver-containing fabrics. Environmental Science and Pollution Research. unpublished.

Lorenz, C., Windler, L., von Goetz, N., Lehmann, R. P., Schuppler, M., Hungerbühler, K., Heuberger, M., and Nowack, B. (2012). Characterization of silver release from commercially available functional (nano)textiles. Chemosphere, 89(7):817–824.

LUX RESEARCH INC (2004). Statement of findings: Sizing nanotechnology's value chain. Technical report.

Migros (2012). Personal communication with migros.

Nightingale, P., Morgan, M., Rafols, I., and van Zwanenberg, P. (2008). Nanomaterials innovation systems: Their structure, dynamics and regulation. Technical report, A Report for the Royal Commission on Environmental Pollution (UK).

Nowack, B., Krug, H. F., and Height, M. (2011). 120 years of nanosilver history: implications for policy makers. Environtal Science and Technology, 45:1177–1183.

Olabarrieta, J., Zorita, S., Peña, I., Rioja, N., Monzó, O., Benguria, P., and Scifo, L. (2012). Aging of photocatalytic coatings under a water flow: Long run performance and tio2 nanoparticles release. Applied Catalysis B: Environmental, 123-124(0):182–192.

Parrish, A. (2010). 2009 record year for nanotechnology patents, 4400+ granted, 49,000+ pending. *http://www.ineffableisland.com/2010/01/2009-record-year-for-nanotechnology.html*, Accessed: 2014-11-19.

Patel, V. (2011). Global carbon nanotubes market - industry beckons. *http://www.nanowerk.com/spotlight/spotid=23118.php*, Accessed: 2014-11-19.

Personal communication with industry people at RAS Materials in Germany (2014).

Piccinno, F., Gottschalk, F., Seeger, S., and Nowack, B. (2012). Industrial production quantities and uses of ten engineered nanomaterials in europe and the world. Journal of Nanoparticle Research, 14(9)(9):1–11.

RAPPORT d'etude (2013). Elements issus des declarations des substances a l'etat nanoparticulaire. Technical report.

Ray, P. C., Yu, H., and Fu, P. P. (2009). Toxicity and environmental risks of nanomaterials: Challenges and future needs. Journal of Environmental Science and Health, Part C, 27(1):1–35.

Robichaud, C. O., Uyar, A. E., Darby, M. R., Zucker, L. G., and Wiesner, M. R. (2009). Estimates of upper bounds and trends in nano-tio2 production as a basis for exposure assessment. Environmental Science & Technology, 43(12):4227–4233.

Roco, M. (2011). The Long View of Nanotechnology Development: The National Nanotechnology Initiative at 10 Years, volume 1 of Science Policy Reports, chapter 1, pages 1–28. Springer Netherlands.

Sahasrabudhe, N. (2010). Chemical information call-in candidate: Nano silver department of toxic substances control. Technical report, San Francisco;.

Scheu, M., Veefkind, V., Verbandt, Y., Galan, E. M., Absalom, R., and Förster, W. (2006). Mapping nanotechnology patents: The epo approach. World Patent Information, 28(3):204–211.

Schmid, K. and Riediker, M. (2008). Use of nanoparticles in swiss industry: A targeted survey. Environental Science and Technology, 42(7):2253–2260.

Streicher-Porte, M. (2014). Ab ins recycling – aber wann? In Fachbericht 2014, pages 17–18. Stiftung Entsorgung Schweiz, Swico and Stiftung Licht Recycling Schweiz.

Sun, T. Y., Gottschalk, F., Hungerbühler, K., and Nowack, B. (2014). Comprehensive probabilistic modelling of environmental emissions of engineered nanomaterials. Environmental Pollution, 185(0):69–76.

The European Commission – Press release database (2013). The common agricultural policy (cap) and agriculture in europe - frequently asked questions. *http://europa.eu/rapid/press-release_MEMO-13-631_en.htm*, Accessed: 2014-11-19.

The Telegraph (2009). Lifespan of energy-saving bulbs reduced by repeated switching. *http://www.telegraph.co.uk/earth/environment/6122459/Lifespan-of-energy-saving-bulbs-reduced-by-repeated-switching.html*, Accessed: 2014-11-19.

U.S. Geological Survey (2014). Silver statistics. Technical report.

von Goetz, N., Lorenz, C., Windler, L., Nowack, B., Heuberger, M., and Hungerbühler, K. (2013). Migration of Ag- and TiO^2-(nano)particles from textiles into artificial sweat under physical stress: Experiments and exposure modeling. Environmental Science & Technology, 47(17):9979–9987.

Wikipedia (2012). European union. *https://en.wikipedia.org/wiki/European_Union*, Accessed: 2017-11-26.

Windler, L., Height, M., and Nowack, B. (2013). Comparative evaluation of antimicrobials for textile applications. Environment International, 53(0):62–73.

Windler, L., Lorenz, C., von Goetz, N., Hungerbühler, K., Amberg, M., Heuberger, M., and Nowack, B. (2012). Release of titanium dioxide from textiles during washing. Environmental Science & Technology.

Zhang, S. and Saebfar, H. (2010). Chemical information call-in candidate: Nano zinc oxide. Technical report, Department of Toxic Substances Control, California, San Francisco.

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